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Life and Chemical Work of Archibald Scott Cooper.

by...

Richard Anschütz

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Life and Chemical Work of Archibald Scott Couper.

By **Richard Anschütz**, Ph.D., LL.D.

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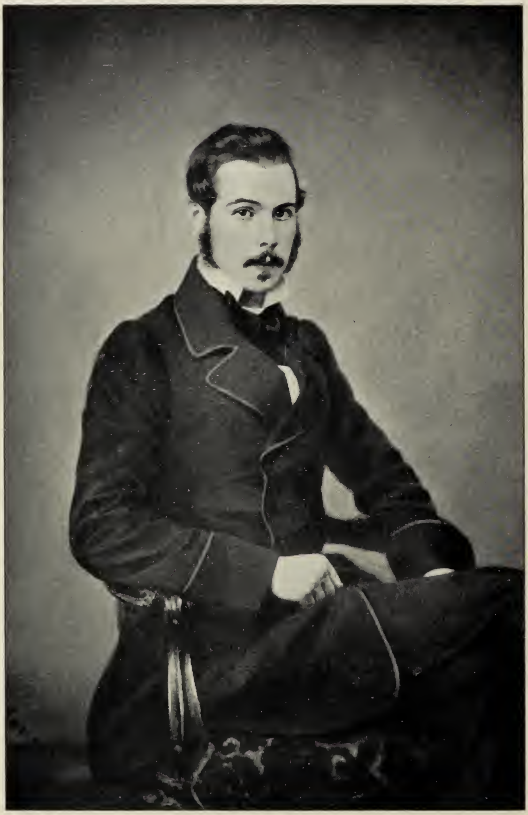

Archd S. Couper

Frontispiece.

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XIII.—Life and Chemical Work of Archibald Scott Couper.

By **Richard Anschütz,** Ph.D., LL.D., Professor of Chemistry in the University of Bonn. *Translated and communicated by* Emeritus-Professor A. Crum Brown, M.D., D.Sc., LL.D.

(MS. received January 25, 1909.)

Preface.

Archibald Scott Couper is one of the most singular appearances in the history of the development of Organic Chemistry in the nineteenth century. He comes on the scene at the time—the end of the 'fifties—when the valency theory began its victorious entrance into our science.

His two experimental investigations, "On some Derivatives of Benzene," and "On Salicylic Acid," as also his communication on "A New Chemical Theory," were published within the limits of one year, and then with startling suddenness his scientific career comes to an end.

Belonging to none of the then existing chemical schools, and furnished with an excellent philosophical training, Couper boldly attacked with sharp criticism the theories prevailing in chemistry at the time.

No claim of priority can be made for his assumption of the concatenation of carbon atoms, but, as will be shown in this paper, his statement was quite independent of that published somewhat earlier by Kekulé.

Without any doubt, Couper deserves the credit of having introduced into constitutional formulæ the lines indicating union of atoms, and of having thus produced what are now called structural formulæ. The results of his work on salicylic acid, long doubted by all the chemists who had repeated his experiments, were at last shown by the present writer to be accurate.

In my efforts to help to his historic rights a fellow-chemist as distinguished as he was unfortunate, and to obtain information as to his origin and life, I have been assisted by my honoured colleagues Heinrich Debus, Greville Williams, Adolf Lieben, Albert Ladenburg, and Alexander Crum Brown. Above all, I have to thank the sympathetic zeal with which Alexander Crum Brown, at my request, gave himself to the discovery of biographical details of his countryman's life. All of that, which I have been able to communicate, as also the translation of this paper into English, is his work.

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Although in physical science there are no national frontiers, still we may expect that the life and achievements of a distinguished investigator will be of special interest to his countrymen. This consideration moved me to offer my paper on the life and chemical work of Archibald Scott Couper to the Royal Society of Edinburgh, and I had the pleasure of seeing it accepted.

Couper's three short papers from the *Comptes rendus de l'Académie des Sciences* have been reprinted here. Couper published his paper on salicylic acid also in English in the *Edinburgh New Philosophical Journal*, adding his new structural formulæ for the derivatives of salicylic acid prepared by him. He gave a full account of his new chemical theory in a paper in the *London, Edinburgh, and Dublin Philosophical Magazine*, and at the same time published a French translation of this paper, with some additions, in the *Annales de chimie et de physique*. I have thought it convenient to print the papers on salicylic acid and the two full accounts of the new chemical theory in both languages, on alternate pages, so as to facilitate reference.

I am hopeful that this unambitious paper may conduce to place the memory of Archibald Scott Couper in its right place in the history of our science, and I thank the Royal Society of Edinburgh for the way in which it has met my endeavour to do this. RICHARD ANSCHÜTZ.

In the history of the development which organic chemistry (or the chemistry of the compounds of carbon) underwent in consequence of the introduction of the hypothesis of the quadrivalence of carbon and the concatenation of carbon atoms, we meet alongside of the conspicuous name of Friedrich August Kekulé that of Archibald Scott Couper.

But Couper had to submit to the hard fortune that his paper "On a New Chemical Theory" was, owing to no fault of his, published too late. It is true that this paper is referred to in chemical history books, but Couper himself fell so completely out of memory that I have not been able to find his name in any of the dictionaries of scientific biography.

As Couper's three papers appeared for the first time, soon after one another, in the *Comptes rendus hebdomadaires des séances de l'Académie des Sciences*, many chemists seem to have taken him for a Frenchman, although his Christian name "Archibald" * points to Scotland, which is indeed his native land.

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* In the *Comptes rendus* the name is given as A. Couper; in the *Annales de chim. et de phys.* as A. S. Couper.

Besides the theoretical paper, Couper published a communication "On some Derivatives of Benzene," and, somewhat later, a very excellent experimental work, "Researches on Salicylic Acid." But just as Couper, through no fault of his, came too late with his theoretical paper, so also with his work on salicylic acid, in which he investigated the action of phosphorus pentachloride on salicylic acid, he had the misfortune that two of the most distinguished German chemists, August Kekulé and Hermann Kolbe, as well as some others, repeated his experiments, but were unable to confirm his results.

Here Couper's appearance in chemistry comes to an end. Although his gifts seemed eminently to qualify him for a brilliant scientific career, no further communication of his is to be found in any scientific journal.

How did this come about? What became of Archibald Scott Couper?

My interest in Couper was first awakened by his work on the action of phosphorus pentachloride on salicylic acid, a subject on which I also was specially engaged. My sympathy with Couper grew when, in the course of the studies required for the preparation of a complete biography of Kekulé, I found it necessary to go very thoroughly into Couper's paper "On a New Chemical Theory." This paper of Couper's must indeed always take its place beside that of Kekulé "On the Constitution and Metamorphoses of Chemical Compounds and on the Chemical Nature of Carbon."

The first information I obtained as to Couper's life was from a letter of Greville Williams, to whom my honoured friend Heinrich Debus applied in order to help me. Some time ago, with Debus' permission, I appended this letter as a note to my paper "On the Action of the Pentachloride and of the Trichloride of Phosphorus on Substituted o-Phenolcarboxylic Acids," published in *Liebig's Annalen*,* and I repeat it here:—

"21 Bournevale Road, Streatham, S.W.,
10*th August* 1903.

"Dear Sir,—I grieve to say that I know nothing of the origin of poor Couper. I first became acquainted with him when I was assistant to Dr (afterwards Lord) Playfair in the University of Edinburgh, where Couper was a student in the laboratory, but he soon left. I only saw him once more, when he came up to me on the seashore at Dunoon on the Clyde, but he was then a complete wreck. I believe his trouble originated in sunstroke. I deeply regret being unable to give you more information about this great but unfortunate genius.—Yours very truly,

"Greville Williams."

---

* cccxlvi. 291 (1906).

At my request Debus now applied to Dr Alex. Crum Brown, Playfair's successor in the Edinburgh Chair of Chemistry. Although the problem seemed hopeless, he attacked it with the greatest earnestness and uncommon skill, and he succeeded.

I am thus enabled to give the following notes of Couper's life, and here thank my honoured friend and distinguished colleague for his kindness in placing in my hands the results of his successful efforts. The communications which I have used in these biographical notes were obtained by Crum Brown in the first place from Couper's cousins, Mrs Little and Miss Tait, Kirkintilloch, and Mr Dollar, the eminent veterinary surgeon, London, and from a university friend of Couper, Mr Berring, Coblenz.

Archibald Scott Couper was born March 31st, 1831, at Townhead,* Kirkintilloch, Dumbartonshire, about six miles north-east of Glasgow. He was the only surviving son of Archibald Couper, proprietor of a large cotton-weaving establishment, employing from 600 to 700 weavers. His mother's maiden name was Helen Dollar. Couper's father inherited the business from his father, who was married to Janet Scott. Couper's second name, "Scott," thus came to him from his paternal grandmother.

There is not much to say about Couper's early youth; it is obvious that he had a good and careful education at home.

In the summer or autumn of 1851 Couper went with his intimate friend, Alexander Hamilton,† to Germany. They had become acquainted in Glasgow, where a similarity of taste in literature and philosophy drew them together. The two young Scotsmen, in a family in Halle to which they had been recommended, applied themselves so diligently to the study of the German language (which is said to be easier for Scotsmen than for Englishmen), that they were soon able to use it with ease.

During the winter session 1851–52, Couper attended Latin and Greek classes in the University of Glasgow.

In the summer of 1852 we again find Couper and Hamilton in Berlin, where Berring‡ made their acquaintance. Berring reports that at that time Couper followed no special line of study, but took a look at various fields of knowledge.

In August 1852 Couper returned to Scotland, and exchanged the University of Glasgow for that of Edinburgh. From this continued university attendance we may conclude that Couper had decided not to follow his father's business, and that his father was pleased to allow his talented son the choice of a learned career.

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* The house, which is in the street, is now converted into shops, and the garden partly covered with buildings.

† Alexander Hamilton, M.A. 1851, D.D. 1872; United Presbyterian minister, Kilmarnock 1855–1872, Brighton 1871–1896. Died at Brighton, 1902.

‡ Afterwards Geheimrat, and director of the engineering works in connection with the navigation of the Rhine.

In Edinburgh the study of philosophy took its place beside that of language. Couper attended the lectures of Sir William Hamilton on logic and on metaphysics, and of Professor MacDougal on moral philosophy. Still Couper does not seem to have taken to chemistry; at least, we find no mention of scientific studies in his notebooks.

Next summer, 1853, Couper and Hamilton returned to Germany and spent some weeks on a visit to Berring's family in Minden, Westphalia. They then made a tour through South Germany, North Italy and the Tyrol, and returned to Scotland.

In the autumn of 1854, or the spring of 1855, Couper came again to Berlin, which evidently had an attraction for him. His friendship with Berring, who was then studying engineering at the "Bauakademie" in Berlin, led the two to take rooms together in a small private hotel, 75 Dorotheenstrasse, where they lived together till Couper left Berlin for Paris in August 1856.

In the meantime Couper had made up his mind for physical science in general and for chemistry in particular. We have no means of knowing what influences or considerations led to this decision, but in any case the turn for chemistry was not present in his early youth, but must have gradually developed during the years of his university life. Berring cannot now with certainty give the name of Couper's teacher of chemistry in Berlin, but he thinks he worked under Rammelsberg. However that may be, there is no doubt that he attended Sonnenschein's lectures on analytical chemistry, and worked for two months in the summer of 1856 in his laboratory. In short, he used the three or four sessions he spent in Germany to perfect himself in analytical chemistry.

While many of his countrymen went to Heidelberg or to Munich, to work under Bunsen or to hear Liebig's lectures, Couper turned to Paris and found a place in Wurtz's laboratory.

In passing, it may be mentioned that in the same year Kekulé began to lecture in Heidelberg, his chemical student days lay behind him when Couper's had just begun.

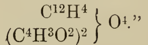
With astonishing rapidity, after only three or four sessions of chemical study, Couper had acquired the knowledge and the skill necessary to enable him to carry out independently experimental chemical investigations.

On Couper's arrival in Paris, Wurtz had just published his brilliant discovery of glycol, by the treatment with caustic potash of the glycol diacetate obtained by the interaction of ethylene iodide and silver acetate. Couper's first work, published in August 1857, is so closely connected with this discovery that one is led to surmise that Wurtz had suggested its subject to Couper—indeed, Couper's paper, "Recherches sur la Benzine,"* immediately follows a paper by Wurtz, "Note sur la liqueur des Hollandais,"† in the *Comptes rendus.*

COUPER'S INVESTIGATIONS ON BENZENE.

Couper started with the supposition that it is possible to convert benzene into the corresponding alcohol and the corresponding glycol. With this view, he treated boiling benzene with bromine vapour and thus discovered brombenzene (boiling point 150°), as well as the dibrombenzene fusing at 89° and boiling at 219°, our *p* dibrombenzene. He nitrated and sulphonised the monobrombenzene. He heated both the brombenzenes to 200° with silver acetate in sealed tubes. He ascertained that monobrombenzene scarcely acts on silver acetate. With better hope of success he tried the action of silver acetate on dibrombenzene, but unfortunately lost his material by an explosion, and had to postpone the continuation of the experiment.

In his communication Couper uses the small equivalents C = 6, O = 8, as Wurtz also always did at that time, and wrote, for instance:—

" Bromobenzine	$C^{12}H^{5}Br$
Dibromobenzine	$C^{12}H^{4}Br^{2}$
Phénylglycol diacétique	 $\left.\begin{matrix} C^{12}H^{4} \\ (C^{4}H^{3}O^{2})^{2} \end{matrix}\right\} O^{4}$."

From this it will be seen that Couper was, at that time, by no means so much under the influence of Gerhardt's type theory as Kekulé was so early as April 1854; see his famous paper, "On a New Series of Sulphurated Acids."‡ He had not, like Kekulé, had the opportunity of developing his scientific opinions by close scientific intercourse with Gerhardt in Paris, and then with Odling, and especially with Williamson in London. No doubt Couper uses for his expected "phénylglycol diacétique" a typical formula; but it is of a sort then generally used even in Germany, and derived from the multiple type of water $H^{2}O^{2}$, and not from the type $H_{2}O$

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* *Comptes rendus*, xlv. 230–232. See Appendix to this paper, p. 235.

† *Ibid.*, xlv. 228–230.

‡ *Proceedings of the Royal Society of London*, vii. 37–40.

of Gerhardt and Williamson. I specially note this point, because Couper, in the new theory which he produced in the course of the next year, freed himself, at least partially, from these erroneous assumptions.

Although Couper's paper "Sur une nouvelle théorie chimique"* appeared somewhat later than his second and last experimental work, "Recherches sur l'acide salicylique,"† I think it more convenient to consider Couper's theoretical views here. For it is not until the close of the paper "On a New Chemical Theory," that Couper applies this theory to salicylic acid, whereas in the French paper on salicylic acid, as also in that on benzene, he uses almost exclusively empirical molecular formulæ.

In order to bring his work before his own countrymen, Couper published a full exposition of his new theory in the *London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science.*‡ He translated this paper into French, and, with some additions, published it in the *Annales de chimie et de physique.*§ He also translated the paper on salicylic acid into English, applying his new theory to the formulation of the derivatives of salicylic acid discussed in it. This translation was printed in the *Edinburgh New Philosophical Journal*, 1858.||

On Couper's New Chemical Theory.

As soon as Kekulé, at that time Privatdocent in Heidelberg, saw Couper's paper in the *Comptes rendus*, he brought forward his claims to the two most important propositions contained in it. Already, in the report of the meeting of the French Academy on the 30th August 1858, we find Kekulé's communication, "Remarques de M. A. Kekulé à l'occasion d'une note de M. Couper sur une nouvelle théorie chimique."¶ We shall therefore most conveniently follow Couper's statements along with Kekulé's remarks on them. In this connection there came to my mind a remark which Kekulé introduced into his speech at the celebration of the twenty-fifth year of the benzene theory, held in Berlin on the 11th of March 1890:** "Some ideas at some time lie in the air: if one does not give expression to them, another will soon do so." Or, as I may add in expansion, different thinkers often come independently and about the same time to proclaim

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* *Comptes rendus*, xlvi. 1157–1160. See Appendix to this paper, p. 237.

† *Ibid.*, xlvi. 1107–1110. See App., p. 266.

‡ xvi. 104–116. See App., p. 240.

§ [3], liii. 469–489. See App., p. 241.

|| viii. 213–217. See App., p. 267.

¶ *Comptes rendus*, xlvii. 378–380.

** *Ber. d. Deutsch. Chem. Ges.*, xxiii. 1304.

the same idea, when the hour of its birth has struck. For, in Couper's paper, "On a New Chemical Theory," the hypothesis of the quadrivalence of carbon and of the concatenation of carbon atoms was developed shortly after the same had been done by Kekulé, and it was—as I have already indicated—only by an accident fateful for Couper that his paper did not appear simultaneously with that of Kekulé, "Über die Constitution und die Metamorphosen der chemischen Verbindungen und die chemische Natur des Kohlenstoffs," * which became so famous.

No doubt Kekulé had already set up the marsh-gas type in his paper on mercuric fulminate, and in a note to the paper, "Über die sogenannten gepaarten Verbindungen und die mehratomigen Radicale," sent to the editors of *Liebig's Annalen* on the 15th of August, 1857, expressed himself thus †:—"Der Kohlenstoff ist, wie sich leicht zeigen lässt und worauf ich später ausführlicher eingehen werde, vierbasisch oder vieratomig d.h. 1 Atom Kohlenstoff = Ͼ = 12 ist äquivalent 4 At. H." In this the hypothesis of the concatenation of carbon atoms was also contained implicitly.

All the same, authentic communications which I have received from highly valued sources leave no doubt that Couper's paper "On a New Chemical Theory" was in the hands of Adolphe Wurtz before the number of *Liebig's Annalen* issued on the 19th of May, and containing Kekulé's paper, dated 16th March, was published. ‡

In a letter dated 29th March 1906, Adolph Lieben writes to me:—

> "Couper's Arbeit ist ganz unabhängig von der Kekulé's, was Niemand besser weiss als ich. Couper, der damals, so wie ich, in Wurtz's Laboratorium arbeitete, war gewöhnt seine Entwürfe und Ideen mit mir durchzusprechen und übergab mir auch, vor der Publication, seine später in den *Compt. rend.* 1858 erschienene Abhandlung zur Prüfung, dann übergab er sie Wurtz. Mittlerweile erschien das Ende Mai ausgegebene Heft der Annalen mit Kekulé's ähnlicher Arbeit und Couper war über dieses Zusammentreffen äusserst bestürzt."

In a letter dated 12th May 1906, Albert Ladenburg gives the following from his recollection:—

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> "Couper arbeitete bei Wurtz in Paris und bat di~~s~~sen seine Abhandlung über die Vierwertigkeit des Kohlenstoffs der Akademie zu überreichen. Wurtz, der damals selbst noch nicht Mitglied war, musste die Abhandlung an einen Anderen der Mitglied war (gewöhnlich Balard) geben. Er verbummelte dies ein wenig und so erschien Kekulé's Mitteilung, ehe die von Couper der Akademie vorgelegt war. Darob grosser Zorn von Couper, der Wurtz zur Rede stellte und ausfällig wurde.

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* *Liebig's Annalen*, cvi. 129–159.

† *Ibid.*, civ. 133, Anm.

‡ *Ibid.*, cvi. 129–159.

Wurtz liess sich das nicht gefallen und verwies ihn aus dem Laboratorium. Couper scheint sich dies sehr zu Herzen genommen zu haben, und in Paris glaubte man den Anfang seiner Krankheit daher zu datieren. Die Geschichte selbst ist authentisch, ich habe sie von Wurtz."

Now that it is thus settled that Couper's paper "On a New Chemical Theory," presented by Dumas to the French Academy, was independent of the corresponding exposition published somewhat earlier by Kekulé, I turn to its contents. It is the case that the line of thought, and so also the mode of expression of the two, have often a startling similarity, though there is no lack of individual peculiarities. Kekulé points out that the opening sentences of Couper's paper—"Je remonte aux éléments eux-mêmes dont j'étudie les affinités réciproques. Cette étude suffit, selon moi, à l'explication de toutes les combinaisons chimiques"—completely agree in meaning with the passage in his own German paper,* which he gives in French thus:—"Je crois nécessaire pour l'explication des propriétés des combinaisons chimiques de remonter jusqu'aux éléments eux-mêmes qui les constituent." A little further on Couper says of carbon: "La puissance de combinaison la plus élevée que l'on connaisse pour le carbone est celle du second degré, c'est-à-dire 4."

To this comes as the second property of carbon: "Il entre en combinaison avec lui-même.

"Ces deux propriétés suffisent à mon avis pour expliquer tout ce que la chimie organique offre de caractéristique. Je crois que la seconde est signalée ici pour la première fois. A mon avis, elle rend compte de ce fait important et encore inexpliqué de l'accumulation des molécules de carbone dans les combinaisons organiques. Dans les composés où 2, 3, 4, 5, 6, etc., molécules de carbone sont liées ensemble, c'est le carbone qui sert de lien au carbone."

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Kekulé seems to have overlooked the fact that Couper does not claim for himself the hypothesis of the quadrivalence of carbon, but only that of the concatenation of the carbon atoms, for he remarks on the passage just quoted (from which he omits the words, "Je crois que la seconde est signalée ici pour la première fois") as follows:—"Nous ne saurions lui accorder que ces propriétés soient signalées par lui pour la première fois. Déjà dans mon premier Mémoire [page 133, note] j'ai dit expressément que le carbone était de nature quatriatomique, c'est-à-dire, que 1 atome de carbone ($C=12$) est équivalent à 4 atomes d'hydrogène ($H=1$), j'ai ajouté que, par conséquent, les combinaisons les plus simples du carbone avec des éléments du premier groupe (éléments monatomiques) étaient CH_4, CCl_4, etc. Dans mon second Mémoire j'ai donné, en outre, plus de développement à cette idée [page 153] et j'en ai tiré comme corollaire [page 154] que dans les substances contenants plusieurs atomes de carbone, on ne peut expliquer cette accumulation que par l'hypothèse que les atomes du carbone lui-même soient liés entre eux, en neutralisant ainsi une partie de leur affinité générale. J'ai cru pouvoir fonder cette hypothèse sur divers exemples trop prolixes pour les rappeler ici; je me contenterai de faire remarquer que, moi aussi, j'ai donné une formule générale qui exprime, pour une certaine classe de combinaisons, le nombre d'atomes d'hydrogène combinés avec n atomes de carbone, dans les termes suivants:

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* *Liebig's Annalen*, cvi. 136.

$$C_nH_{n(4-2)+2}\text{,*}$$

tandis que M. Couper, de son côté, l'exprime de cette manière:

$$C_nM_{n.4} - M_{m.2} = nCM_4 - mM_2$$

où m est $<n$."

It seems to me that Kekulé has misunderstood Couper's general formulæ, for Couper expressly says:—"Toutes les combinaisons du carbone peuvent être ramenées à deux types. L'un d'eux est représenté par le symbole

$$nCM^4$$

l'autre par le symbole

$$nCM^4 - mM^2$$

où m est $<n$, ou bien

$$nCM^4 + mCM^2$$

où n peut devenir nul. On peut citer, comme exemple du premier type, les alcools, les acides gras, les glycols, etc."

Now, if the alcohols, the fatty acids, the glycols, etc., are examples of Couper's first type, so that all saturated compounds were obviously included by him under that type, I can understand this only by assuming that M does not represent the atom of a univalent element, but the valency engaged. Only on that assumption is nCM^4 the expression for all saturated carbon compounds. And the expression $nCM^4 - mM^2$ is then the general form for the formulæ of the unsaturated carbon compounds. Couper places beside it the form $nCM^4 + mCM^2$. The unsaturated carbon compounds, those which, to use a later form of speech, contain doubly and trebly united carbon, can be brought under this form. Carbonic oxide can be derived from either of the two, if we put $n = m = 1$ in the first, or $n = 0$ and $m = 1$ in the second.

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* Misprinted in the *Comptes rendus* "$C_nH_{n(1-2)+2}$." See *Liebig's Annalen*, cvi. 154.

Founding on his mode of regarding combination, Couper writes formulæ in which the mutual bonds of the atoms are indicated by means of connecting lines, dotted in the papers in the *Comptes rendus* and in the *Philosophical Magazine*, continuous in that in the *Annales de chimie et de physique*—true structural formulæ in our present meaning of the term.

Kekulé, in his derivation of the constitution of the radicals, resolved the formulæ as completely as Couper; but when he had done this in words, he put the contracted radical formulæ into typical formulæ. He thus retained Gerhardt's mode of writing, and developed the idea of the typical formulæ. In the first part of his textbook, issued in the spring of 1859, he gave a graphic representation of the mode of union of the atoms, but undoubtedly our present manner of writing structural formulæ was started by Couper.

There is, however, one point on which Kekulé expressly establishes a difference between his view and that of Couper. Couper speaks, in a passage quoted above, of "la puissance de combinaison la plus élevée que l'on connaisse pour le carbone." He distinguishes two kinds of affinity in an element:—

"1. L'affinité de degré,
2. L'affinité élective."

What Couper wished to be understood by "l'affinité de degré" is explained by reference to carbon:—

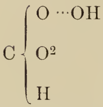
"Prenant pour exemple le carbone, je trouve qu'il exerce son pouvoir de combinaison en deux degrés. Ces degrés sont représentés par CO^2 et CO^4, c'est-à-dire par l'oxyde de carbone et l'acide carbonique, en adoptant pour les équivalents du carbone et de l'oxygène les nombres 12 et 8."

Without discussing the example chosen by Couper to explain the "affinité de degré," Kekulé says:—"Si M. Couper croit avoir découvert la cause de cette différence de basicité dans l'existence d'une espèce speciale d'affinité, l'affinité de degré, je suis le premier à reconnaître que je n'ai aucun droit à lui contester cette priorité."

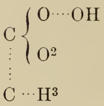
But Couper's "affinité de degré" is obviously nothing else than what was afterwards called "variable valency," and the passage quoted above from Kekulé's claim of priority is his first clear expression of his disbelief in variable valency.

That Couper assumes $O=8$, while he puts $C=12$, is an inconsistency to which Kekulé makes no reference; I shall return to this matter later.

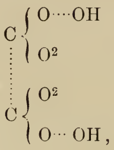
Couper writes the formulæ of formic acid, acetic acid, and oxalic acid thus:—



$$C\left\{\begin{array}{l} O\cdots OH \\ O^2 \\ H \end{array}\right.$$

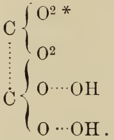


$$\begin{array}{l} C\left\{\begin{array}{l} O\cdots OH \\ O^2 \end{array}\right. \\ \vdots \\ C\cdots H^3 \end{array}$$



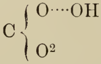
$$\begin{array}{l} C\left\{\begin{array}{l} O\cdots OH \\ O^2 \end{array}\right. \\ \vdots \\ C\left\{\begin{array}{l} O^2 \\ O\cdots OH, \end{array}\right. \end{array}$$

or the latter, "Si l'on veut réunir l'oxygène négatif à l'un des poles de la molécule, par la formule:—



$$\begin{array}{l} C\left\{\begin{array}{l} O^2\,* \\ O^2 \end{array}\right. \\ \vdots \\ C\left\{\begin{array}{l} O\cdots OH \\ O\cdots OH. \end{array}\right. \end{array}$$

Couper attaches to this a remark on the electronegative or electropositive state of the oxygen atoms that are united in the group



$$C\left\{\begin{array}{l} O\cdots OH \\ O^2 \end{array}\right.$$

The oxygen atoms are in general in an electronegative state. But one oxygen atom—that one which is united to an electropositive element, such as hydrogen—thus takes on an electropositive state. The presence of the other two oxygen atoms united to carbon is necessary in order to bring the negative oxygen into the state which gives the substance the properties which are usually designated by the term acid.

He adds: "Ceci est un cas particulier d'une loi générale; car on peut voir, d'après cette théorie, comment la valeur électropositive ou électronégative des éléments modifie et conditionne mutuellement la valeur électropositive ou électronegative des autres éléments."

At the close of his paper Couper deduces from his new views the formulæ of salicylic acid and of the substance formed from it by the action of phosphorus pentachloride, to which he gave the name "trichlorophosphate de salicyle." I shall postpone the consideration of these formulæ till I have explained the reaction itself, and now turn to Couper's fuller English paper "On a New Chemical Theory." The French version of this paper, which appeared soon after the publication in the *Philosophical Magazine*, is by Couper himself, and contains some additions made by him.

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* In the *Comptes rendus* "C^2" is printed in error for "O^2."

Both give us a much deeper view into Couper's mode of thought. They show us how powerfully he was affected by his early philosophical training. In the introduction he developes in a general way the conditions which every sound theory must fulfil. The English paper begins with the two propositions: "The end of chemistry *is its theory*. The guide in chemical research *is a theory*." These he translates in the French version:—

"L'étude de la chimie doit avoir pour but l'établissement de la théorie de cette science; une théorie elle-même est un guide qui nous conduit dans les recherches chimiques."

Couper then criticises the theories prevalent at that time, especially Gerhardt's type theory as the most important, but also the radical theory and the theory of copulæ. He rejects them all. He objects to the type theory that the peroxides do not fit into the types. Gerhardt's types are, as he himself says, types of double decomposition, but we cannot regard as double decomposition such actions as the formation of sulphuric acid from its anhydride and water. The multiple water types existed only in Gerhardt's imagination.

Couper now examines in how far Gerhardt's type theory is in accordance with the fundamental requirements of philosophy, which demand that it should explain the greatest number of facts in the simplest possible way. In the next place, a test must be applied to see if it explains the facts at all; and thirdly, if that is so, how it explains them.

To these questions Couper answers that Gerhardt's type theory does indeed, from a certain point of view, compare every chemical compound with every other, but that it does not explain the facts at all, so that obviously the how of the third question has no application.

Couper's sarcastic vein appears in a remarkable parallel which he draws in order to show the absurdity of the type theory:—"Suppose that some one were to systematize the formation of letters into words that formed the contents of a book. Were he to begin by saying that he had discovered a *certain word which would serve as a type, and from which by substitution and double decomposition all the others are to be derived*,—that he, by this means, not only could form new words, but new books and books almost *ad infinitum*,—that this word also formed an admirable point of comparison with all the others,—that in all this there were only a few difficulties, but that these might be ingeniously overcome,—he would state certainly an empirical truth. At the same time, however, his method would, judged by the light of common sense, be an absurdity. But a principle which common sense brands with absurdity is philosophically false and a scientific blunder."

The following considerations may be regarded as the outcome of his philosophical studies at the university:—"The sure and invincible method of arriving at every truth which the mind is capable of discovering is always one and the same. It is that, namely, of throwing away all generalization, of going back to first principles, and of letting the mind be guided by these alone. . . . To reach the structure of words we must go back . . . to the letters. . . . In mathematics the starting-point is not generalizations, but axioms. . . . In metaphysics Descartes led the way of progress by analysing till he thought he could reach some ultimate elements beyond which it was impossible for him to go, then studying their force and power, and proceeding synthetically. . . . On the other hand, . . . Gerhardt's generalization . . . leads him . . . to restrict chemical science to the arrangement of bodies according to their decomposition, and to deny the possibility of our comprehending their molecular constitution."

Couper examines less fully the radical theory and the theory of copulæ. The radical theory ascribes to the radicals the character of elements, of ultimate powers, and thus stops at the very point where an explanation is required. The theory of bodies conjugated by addition divides chemical compounds, if possible, into two parts, but gives no account of the force which holds these parts together.

We cannot but see that it is, for Couper, a philosophical necessity, in seeking an explanation of the molecular structure of chemical compounds, to go back to the chemical elements of which they are composed, and in the very first place to find out the properties and functions of these elements. The whole of chemistry must, he says, be considered as one. The general principles common to all the elements and those peculiar to each must be determined. In each known chemical compound the properties and relations of each element contained in it must be taken into consideration.

After this philosophical introduction Couper developes his theory, establishing individual points more fully here than in the short communication in the *Comptes rendus.* Nowhere does the contrast in the mode of thought between Couper and Kekulé appear more clearly than in the philosophical foundation which Couper gives to his theory, rejecting Gerhardt's type theory, the radical theory, and the theory of copulæ. Kekulé, as is well known, deduced his valency theory as the idea lying at the root of Gerhardt's type theory, as he himself puts it, as a conscious, immediate development of Dalton's atomic theory, without severing the connection with the type theory and the radical theory.

Couper's complete French paper called forth the opposition of Alexander Butlerow. In a paper in *Liebig's Annalen*, entitled "Bemerkungen über A. S. Couper's neue chemische Theorie,"* he finds fault with Couper's statement, "Die Aufstellung einer Theorie" "ist der Zweck wissenschaftlicher Untersuchungen."† This translation of Butlerow's is not quite accurate; the French sentence is: "L'étude de la chimie doit avoir pour but l'établissement de la théorie de cette science." The English paper in the *Philosophical Magazine*, which Butlerow does not seem to have known, begins, as already stated, with the sentence: "The end of chemistry is its theory." "Meiner Ansicht nach," says Butlerow, "ist die Ausbildung einer Theorie die notwendige Folge vorhergegangener Untersuchungen, der Zweck aber ist eher die Kenntniss der Gesetze, nach welchen chemische Metamorphosen vor sich gehen." Couper would certainly not have disputed the statement that chemical investigations ought to teach us laws, but laws have to be explained, and to do that there is need of hypothesis or theory. Thus the ultimate aim remains still the establishment of a theory, which makes the laws intelligible, as Dalton's atomic theory did for the laws of constant composition and of multiple proportions.

I am inclined to think that the chief inducement for Butlerow to occupy himself with Couper's new theory was the opportunity of stating that nine months before, that is, early in March (his paper is dated Kazan, 1/13 December 1858), he had communicated similar theoretical views to members of the Chemical Society of Paris, although he had not then printed them. He repeats what he then said as follows:—"Wenn man unter den Radicalen nur Reste versteht, welche ihre Constitution in einer gewissen Anzahl der Reactionem beibehalten, n so können mit demselben Rechte, wie die organischen Gruppen und Elemente, auch die Reste

$$\mathrm{HO_2 \text{ vom Typus} \left.\begin{matrix} H \\ H \end{matrix}\right\} O_2}\,\dagger,\ \mathrm{NH_2 \text{ vom Typus} \left.\begin{matrix} H \\ H \\ H \end{matrix}\right\} N}$$

als Radicale betrachtet werden, und man könnte annehmen, dass sie ein Atom eines Elementes in verschiedenen Gruppen substituiren können. In diesem Sinne würde man zum Beispiel folgende Körper als zu einem und demselben Typus der Molecularstructur gehörend ansehen:

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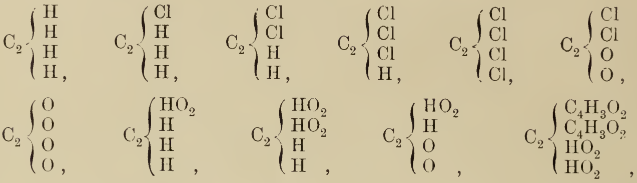
* cx. 51–66 (Heft 1, issued 16th April 1859).

† "Wie es Laurent annahm."



$$C_2\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right., \quad C_2\left\{\begin{matrix}Cl\\H\\H\\H\end{matrix}\right., \quad C_2\left\{\begin{matrix}Cl\\Cl\\H\\H\end{matrix}\right., \quad C_2\left\{\begin{matrix}Cl\\Cl\\Cl\\H\end{matrix}\right., \quad C_2\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right., \quad C_2\left\{\begin{matrix}Cl\\Cl\\O\\O\end{matrix}\right.,$$

$$C_2\left\{\begin{matrix}O\\O\\O\\O\end{matrix}\right., \quad C_2\left\{\begin{matrix}HO_2\\H\\H\\H\end{matrix}\right., \quad C_2\left\{\begin{matrix}HO_2\\HO_2\\H\\H\end{matrix}\right., \quad C_2\left\{\begin{matrix}HO_2\\H\\O\\O\end{matrix}\right., \quad C_2\left\{\begin{matrix}C_4H_3O_2\\C_4H_3O_2\\HO_2\\HO_2\end{matrix}\right.,$$

u.s.w., u.s.w."

From these formulæ we see that Butlerow was at that time still an adherent of the small atomic weights, or equivalents, for carbon $C = 6$, and for oxygen $O = 8$. He had thus, in this respect, remained behind Kekulé, and, so far as carbon is concerned, behind Couper also.

Couper set up, as I have already pointed out, two types for all carbon compounds, which, at the beginning of his complete paper, he formulates as follows (still with $C = 6$):—

$$nC^2M^4$$
$$nC^2M^4 - mM^2.^*$$

Further on he adopts $C = 12$ for the following reasons: "There is no reaction found where it is known that C^2 is divided into two parts. It is only consequent therefore to write, with Gerhardt, C^2 simply as C, it being then understood that the equivalent of carbon is (12) twelve."

The two types then take the forms exclusively used by Couper in his short paper in the *Comptes rendus*:—

$$nCM^4$$
$$nCM^4 - mM^2$$

where m is less than n.

Butlerow had difficulty in understanding these two formulæ. I give here his criticism: "Setzt man in dem ersten von Couper vorgeschlagenen Ausdruck nC_2M_4 z.B. $n = 6$, so wird man $C_{12}H_{24}$ haben; die Grenze des Verbindungsvermögens für das complexe Kohlenstoffmolecul C_{12} ist aber M_{14} (allgemeiner Ausdruck $= C_{2n}M_{2n+2}$).† Will man die typische Formel von Couper mit den Thatsachen in Übereinstimmung bringen, so muss man unter nM_4 Affinitätseinheiten verstehen, und zu denselben die Affinität des Kohlenstoff selbst (zwei Affinitätseinheiten für jedes Molecul C_2), ausser der, die einem Molecule C_2 gehört, mitrechnen." As already ex-

* In the *Phil. Mag.* misprinted $nC^2M^4 - mM$. See *Ann. de chim. et phys.* (3), liii. 480, line 10 from top.

† Butlerow has obviously here in mind Kekulé's general expression C_nH_{2n+2}.

plained, I completely agree with Butlerow in this interpretation of nM_4. But if we make this assumption for the type nC_2M_4 ($=nCM_4$), we must do the same for the second type $nC_2M_4 - mM_2$, and that is what Butlerow does not do, for he says of this type:—“Die zweite typische Formel $nC_2M_4 - mM_2$” ($nCM^4 - mM^2$) “wenn der Strich (–) das Zeichen der Verbindung vorstellen soll, wie in anderen Formeln von Couper, stimmt mit den Thatsachen auch nicht überein; soll sie aber als nC_2M_4 minus mM_2 verstanden werden, so bekommt man für $n=7$, $m=6$ z.B. $C_{14}H_{28} - 12H = C_{14}H_{16}$, das heisst eine Verbindung mit der möglichst grossen Menge von Wasserstoff.—Die Verbindung $C_{12}H_6$ aber, ihre Homologen, Naphtalin, u.s.w. wo der Verbindungsgrad nicht der Formel $C_{2n}H_{2n+2}$ und sogar nicht der Proportion $C_{2n}H_{2n}$ entspricht, durch welche allgemeine Formeln sollen sie vorgestellt werden?”

Kekulé also, as I have shown above, misunderstood the expression.

I note first that in the formula the stroke (–) is clearly a minus sign and not a mark of combination. If we keep in view that the first term of the second type is identical with the first type, and must have the same meaning, so that M stands for a unit of affinity, then we see that nCM^4 is the type for all saturated carbon compounds in the second type also. If then nM^2 units of affinity are to be subtracted from nCM^4 (because they are not saturated), the expression $nCM^4 - mM^2$ is the type of those carbon compounds which we call unsaturated. Benzene and naphthalin, the examples chosen by Butlerow, can be referred without any difficulty to this type. Let $n=6$ and $m=4$, then, if no element but hydrogen is present with the carbon, we have:

$$\begin{array}{l} nCM^4 - mM^2 \\ C_6H_{14} - 8H = C_6H_6 = \text{Benzene.} \end{array}$$

Let $n=10$ and $m=7$, then we have

$$\begin{array}{l} nCM^4 - mM^2 \\ C_{10}H_{22} - 14H = C_{10}H_8 = \text{Naphthalin.} \end{array}$$

In the first case supposed by Butlerow, on the assumption of $n=7$ and $m=6$, we should have for

$$\begin{array}{lll} & nCM^4 - mM^2 & \\ & (\text{or}\quad nC_2M^4 - mM^2) & \\ \text{not} & C_7H_{28} - 12H = C_7H_{16} & (\text{or } C_{14}H_{28} - 12H = C_{14}H_{16}) \\ \text{but} & C_7H_{16} - 12H = C_7H_4 & (\text{or } C_{14}H_{16} - 12H = C_{14}H_4). \end{array}$$

That would be a formula in which 7C (or $7C^2$) are united by 12 carbon affinities, leaving 4 affinities over for union with hydrogen.

The most difficult thing to understand in Couper's view is how he comes to the conclusion that the equivalent, atom or molecule (he does not distinguish between these terms), of oxygen must be taken as 8 and not as 16. It seems to me that Couper, still entangled in the doctrine of Berzelius, considered the hydrates of the oxygen acids and the salts of these acids as composed of two electrically opposite components. He takes a hydrated acid as a compound of the anhydride and water. In the formation of a salt from a hydrated acid and a basic hydroxide, according to him, it is not the hydrogen of the acid which changes place with the metal of the basic hydroxide, but the hydrogen takes with it an atom of oxygen ($O=8$) from the acid, and the metal carries an oxygen atom from the basic hydroxide into the salt. The oxygen atom of the acid radical, with which is united the oxygen atom combined with the metal, is negative, while the latter oxygen atom is rendered positive by its union with the metal. The reaction between hydrated acid and basic hydroxide is possible because the affinity between the positive and the negative oxygen is less than that between metal and oxygen, hydrogen and oxygen, and acid residue and oxygen. "A consequence of this truth is, that it is impossible to double the equivalent of oxygen, if the chemical equivalents are to be understood as not being in direct contradiction to any chemical truth or essential feature in the properties of an element. Carbon differs entirely in this respect from oxygen."

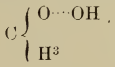
If Couper had not been so fundamentally opposed to Gerhardt's type theory he would no doubt have freed himself from these untenable views. Butlerow, too, thought Couper's adherence to the equivalent 8 for oxygen unfounded. He sets against Couper's notion of double decomposition that of Kekulé, according to which the two interacting molecules, in the first moment of the reaction, unite, and then the resulting complex splits in a new direction.

In Couper's three papers there are to be observed some variations in the mode of writing the examples of constitutional formulæ of carbon compounds. In the first short note in the *Comptes rendus,* dotted lines and brackets are used to indicate the bonds. Brackets are also used in the fuller paper in the *Annales de chimie et de physique,* with continuous instead of dotted lines. In the use of brackets we can well see a concession to the French and German chemists, who had been accustomed to their use by Gerhardt. In the English paper in the *Philosophical Magazine* the dotted lines are retained and the brackets are altogether discarded.

I here give Couper's constitutional formulæ for carbon compounds containing oxygen, from the *Comptes rendus* paper, in which he takes

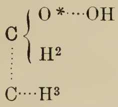
$C=12$ and $O=8$ throughout. I here omit the formulæ of salicylic acid and the products obtained from it by means of phosphorus pentachloride, as these will be discussed under the next head.

Methyl Alcohol.



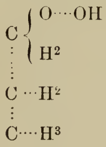
$$C\begin{cases} O\cdots OH \\ H^3 \end{cases}$$

Ethyl Alcohol.



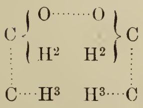
$$\begin{array}{l} C\begin{cases} O^{*}\cdots OH \\ H^2 \end{cases} \\ \vdots \\ C\cdots H^3 \end{array}$$

Propyl Alcohol.



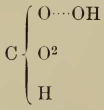
$$\begin{array}{l} C\begin{cases} O\cdots OH \\ H^2 \end{cases} \\ \vdots \\ C\cdots H^2 \\ \vdots \\ C\cdots H^3 \end{array}$$

Ethyl Ether.



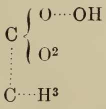
$$\begin{array}{lcr} C\left\{\begin{array}{l} O \\ H^2 \end{array}\right. & \cdots\cdots & \left.\begin{array}{r} O \\ H^2 \end{array}\right\}C \\ \vdots & & \vdots \\ C\cdots H^3 & & H^3\cdots C \end{array}$$

Formic Acid.



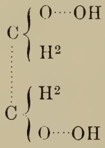
$$C\begin{cases} O\cdots OH \\ O^2 \\ H \end{cases}$$

Acetic Acid.



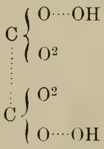
$$\begin{array}{l} C\begin{cases} O\cdots OH \\ O^2 \end{cases} \\ \vdots \\ C\cdots H^3 \end{array}$$

Glycol.



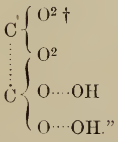
$$\begin{array}{l} C\begin{cases} O\cdots OH \\ H^2 \end{cases} \\ \vdots \\ C\begin{cases} H^2 \\ O\cdots OH \end{cases} \end{array}$$

Oxalic Acid.



$$\begin{array}{l} C\begin{cases} O\cdots OH \\ O^2 \end{cases} \\ \vdots \\ C\begin{cases} O^2 \\ O\cdots OH \end{cases} \end{array}$$

"Ou, si l'on veut réunir l'oxygène négatif à l'un des poles de la molécule, par la formule



$$\begin{array}{l} C\begin{cases} O^{2}\dagger \\ O^2 \end{cases} \\ \vdots \\ C\begin{cases} O\cdots OH \\ O\cdots OH." \end{cases} \end{array}$$

In the two full papers Couper then gives quite a number of constitutional formulæ with $C=6$; these I omit. Then he explains why C should be taken $=12$, but he retains, as I have already more than once stated, $O=8$. I now give, in three columns:—1st, the formulæ from the *Annales de chimie et de physique* paper; 2nd, those from the *Philosophical Magazine* paper; 3rd, the formulæ obtained from these by putting $O=16$. While in the *Comptes rendus* paper Couper contented himself with quite simple examples, in the fuller papers he gives formulæ for substances with a more complicated composition.

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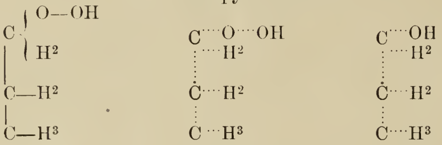
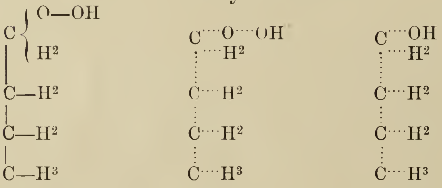
* In the paper the first "O" has been omitted in error.

† Misprinted "C^2" for "O^2" in the paper.

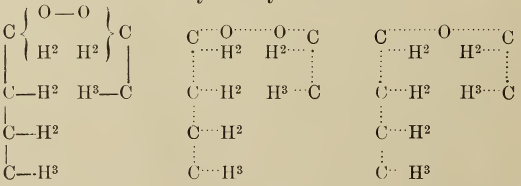
Propyle Alcohol.



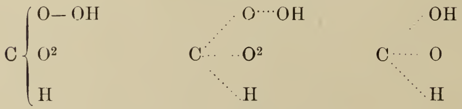
Butyle Alcohol.



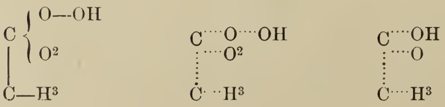
Butylic-ethylic Ether.



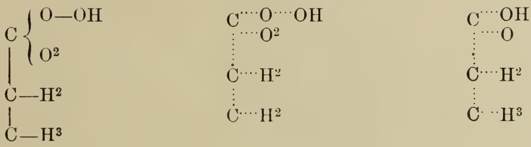
Formic Acid.



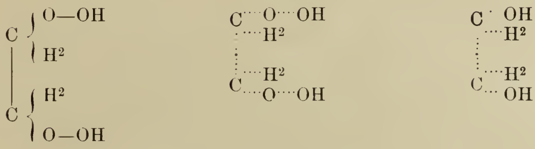
Acetic Acid.



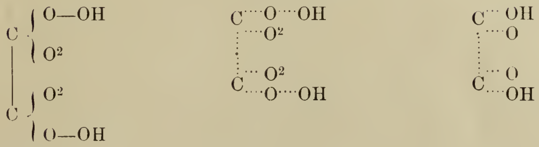
Propionic Acid.



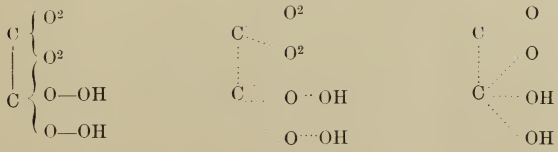
Glycol.



Oxalic Acid.



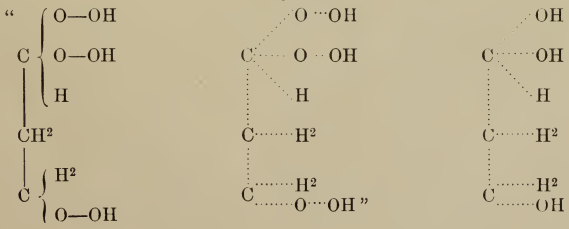
or, as before,



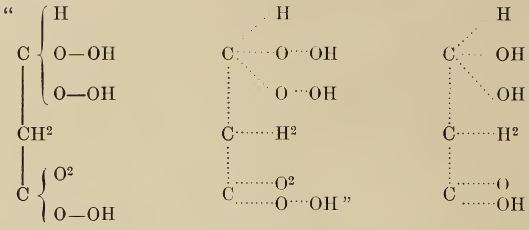
Couper thus gives an alternative formula for oxalic acid, in which the two (...O...OH) groups are united to one and the same carbon atom.

While Couper's formulæ, with the exception of this last, pass immediately into the constitutional formulæ now in use, if we take O = 16, he is less happy in formulating glycerin and glyceric acid.

Glycerin.

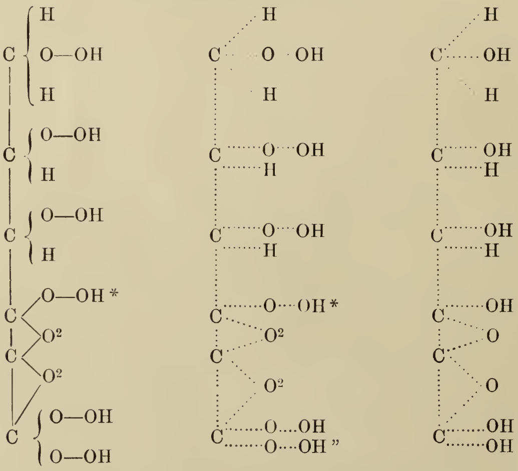


Glyceric Acid.

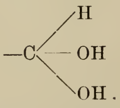


“Glucose has been perhaps too little investigated to afford data sufficient to determine definitely its formula. Taking, however, mucic and saccharic acids as starting-points, these bodies may be meanwhile represented as:—

Mucic and Saccharic Acids.



The error here is, essentially, the application to mucic and saccharic acids of the second possible mode of formulating oxalic acid, with the two acid hydroxyls on the same carbon atom. On the other hand, the formula for glucose is right, if we suppose the aldehyde group $-CHO$ transformed, by the addition of water, into the group



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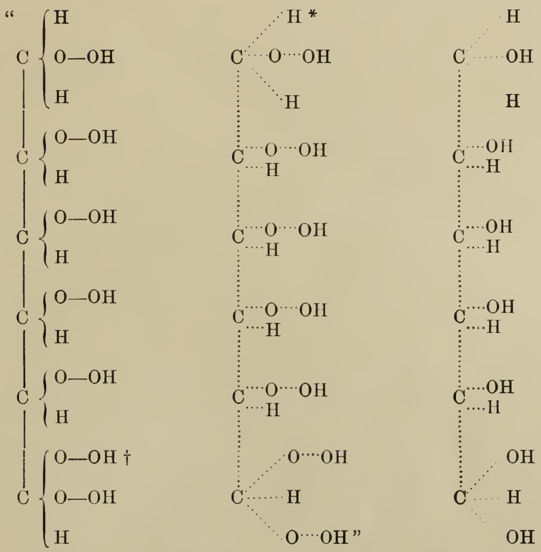
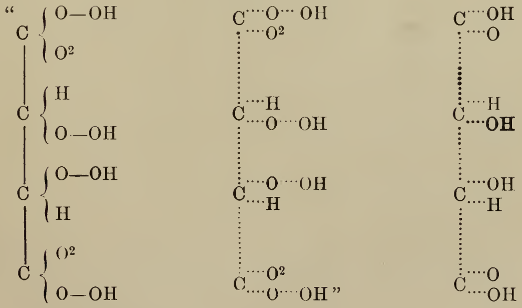
* In the papers this “OH” has been omitted in error.

Glucose.



Couper's formula for tartaric acid is, if we put O = 16, identical with our structural formula for that acid, as here Couper distributes the two acid hydroxyls to the two end carbon atoms.

Tartaric Acid.



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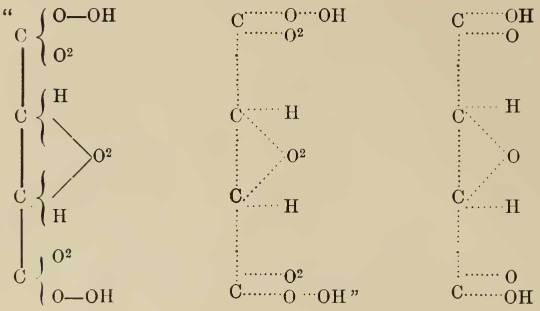
* In this formula the dotted lines joining the six carbon atoms have been omitted in the paper.

† Misprinted “H” for “O—OH.”

For tartrelic acid, formed by loss of water from tartaric acid, Couper gives the following formula:—

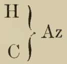
Tartrelic Acid.



All these compounds belong, according to Couper, to the type nCM^4.

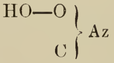
At the close of his paper in the *Philosophical Magazine*, Couper expresses his intention to discuss, in a later paper, the second type ($nCM^4 - mM^2$) and to apply his principles to the cyanogen compounds. His paper in the *Annales de chimie et de physique* closes with formulæ for hydrocyanic acid, cyanic acid, and cyanuric acid:—

Hydrocyanic acid



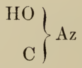
$$\left.\begin{matrix}H\\C\end{matrix}\right\}Az$$

Cyanic acid



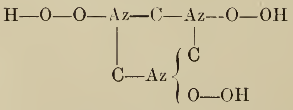
$$\left.\begin{matrix}HO{-}O\\C\end{matrix}\right\}Az$$

or, with $O = 16$,

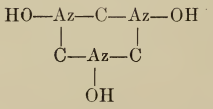


$$\left.\begin{matrix}HO\\C\end{matrix}\right\}Az$$

Cyanuric acid

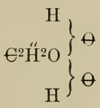


or, with $O = 16$,



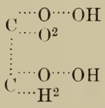
Thus in cyanuric acid Couper assumed that the three carbon atoms and the three nitrogen atoms are combined alternately in ring form.

By his method of writing formulæ Couper took an important step forward. His formulæ, in fact, enabled him, in a simple and clear way, to express his views as to the mutual combination of the atoms in the molecules of chemical compounds. Kekulé still, at that time, made shift, if we may use the expression, with typical formulæ. Although his ideas were no less clear than those of Couper, yet the formulæ he used were still quite those of the type theory. He wrote glycollic acid :—



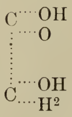
$$\begin{matrix}\mathrm{H} & \\ & \Big\}\,\Theta \\ \text{Є}^2\overset{\prime\prime}{\mathrm{H}}{}^2\mathrm{O} & \\ & \Big\}\,\Theta \\ \mathrm{H} & \end{matrix}$$

deriving it from the double water type. Couper, as is clearly shown by his tartaric acid formula, would have written glycollic acid thus :—



$$\begin{array}{l}\mathrm{C}\cdots\mathrm{O}\cdots\mathrm{OH}\\ \vdots\cdots\mathrm{O^2}\\ \vdots\\ \vdots\cdots\mathrm{O}\cdots\mathrm{OH}\\ \mathrm{C}\cdots\mathrm{H^2}\end{array}$$

and from this we at once get our present structural formula for glycollic acid :—



$$\begin{array}{l}\mathrm{C}\cdots\mathrm{OH}\\ \vdots\cdots\mathrm{O}\\ \vdots\\ \vdots\cdots\mathrm{OH}\\ \mathrm{C}\cdots\mathrm{H^2}\end{array}$$

It was not until the spring of 1859 that Kekulé, in the first part of his *Lehrbuch*, in remarks on the mutual union of atoms, gave his well-known graphic representation in which the basicity of the atoms is indicated by a difference in the size of their symbols—a difference in size which, as Kekulé expressly says, is not intended to express any difference in the actual size of the atoms, but only the number of chemical units which an atom represents, that is, the number of hydrogen atoms to which it is equivalent.

We have already become acquainted with Butlerow's remarks on Couper's new chemical theory. But before him, immediately after the appearance of Couper's paper in the *Annales de chimie et de physique*, Wurtz expressed his views in reference both to Kekulé's paper, " Über die Constitution und die Metamorphosen der chemischen Verbindungen und über die chemische Natur des Kohlenstoffs," * and to Couper's " Sur une nouvelle théorie chimique."† His remarks were published in the *Répertoire de chimie pure et appliquée*, a journal he had just founded for notes on current chemical literature. The distinguished position of Wurtz, and his relation to Couper, make his criticism specially worthy of our consideration.

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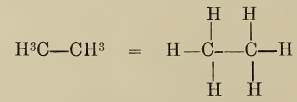
* Rép. 20–24.

† Rép. 49–52.

After a short note of the contents of the paper, he combats Couper's assumption of O = 8, and says: "Cette théorie électrochimique d'un nouveau genre aurait besoin de s'appuyer sur quelques faits."

But there is not wanting a word of recognition by Wurtz:—"Je dois faire remarquer encore que les idées énoncées par M. Couper et qui me paraissent ingénieuses et acceptables, si on les dégage certaines hypothèses accessoires et de quelques nuages qui en enveloppent l'exposition, ne sont nullement en contradiction avec la doctrine des radicaux, et même avec cette des types moléculaires contre lesquelles l'auteur a cru devoir rompre une lance." Wurtz closes his notice with the following statement of opinion:—"En général, je trouve les formules de M. Couper trop arbitraires, trop éloignees de l'expérience. Par nos formules rationnelles nous n'avons pas la prétention de représenter la constitution intime des combinaisons. Ces formules ne représentent que les métamorphoses, c'est-à-dire des faits accessibles à l'expérience et demontrés par elle. Voilà leur avantage. Dans les formules de M. Couper, au contraire, la place de chaque atome se trouve marquée, non seulement par le pouvoir basique des éléments, mais encore par je ne sais quelle attraction électrique ou polaire. C'est trop d'hypothèses, et l'on a tort de nous présenter toutes ces choses comme la loi et les prophètes. A cet égard, M. Kekulé, qui me parait avoir mieux compris le sens et la portée des idées, qu'il a énoncées le premier, a dit sagement à la fin de son Mémoire: 'Pour mon compte, je n'attache qu'une importance secondaire à des considérations de cet ordre là.'"

And here Wurtz should not have let the opportunity slip of putting it on record that Couper had given him the MS. of his paper for the *Comptes rendus* before Kekulé's paper appeared in *Liebig's Annalen*. Further we may note how Wurtz expressed himself some years later as to formulæ in which, exactly as had been first proposed by Couper, the mutual relations of the atoms forming a compound were represented by means of lines joining the symbols. In his work, *La théorie atomique*, Paris, 1879, livre ii., "Atomicité, ou valence des atomes dans les combinaisons," Wurtz discusses very fully the distribution of the hydrogen atoms in ethane, and says (p. 156): "Telle est la signification de la formule:



$$H^{3}C—CH^{3} \;=\; H—\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}——\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}—H$$

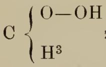
dans laquelle cet échange d'unités de saturation est marqué par les traits qui séparent les lettres." To this he appends a note:—"Cette notation généralement usitée aujourd'hui a été employée pour la première fois dans les leçons que j'ai faites au Collège de France pendant l'été de 1863, et qui ont été publiées d'abord dans le *Moniteur scientifique* du Dr Quesneville, et plus tard sous le titre *Leçons de philosophie chimique*, Hachette, 1864. Je renvoie à cet égard aux pages 140, 143, 145, 158 et 182 de cet opuscule." When Wurtz wrote these lines he had evidently forgotten the formulæ in Couper's paper which he had condemned as too fantastic.*

Butlerow, Couper's other critic, returns to the question in 1868,† about ten years later, after organic chemistry had undergone so mighty a development under the influence of the valency theory, and now fully recognises Couper's position. He says:—"Dass ferner die von Couper (leider nur kurz) ausgesprochenen Ansichten, mit den jetzt fast allgemein anerkannten identisch sind, verneine ich nicht, und sicher sind die von Couper gegebenen Formeln rationelle Formeln im gegenwärtigen Sinne des Wortes, d.h. Constitutionsformeln oder Formeln chemischer Structur."

I shall now sum up the results. It is quite certain that Kekulé proclaimed the hypothesis of the quadrivalence of carbon and the concatenation of carbon atoms before Couper. In contrast to Kekulé, Couper started the idea of affinity of degree in chemical elements, and illustrated it by the examples of carbonic oxide and carbonic acid. In the former he regarded carbon as bivalent, in the latter as quadrivalent, thus recognising a change of atomicity or valency.

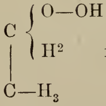
Albert Ladenburg, in his lectures *On the Development of Chemistry during the last Hundred Years*, published in 1869, refers as follows to Couper's formulæ:—‡ "Hier begegnen wir zum ersten Male Constitutionsformeln im heutigen Sinne des Worts, Symbolen, welche aus der Erkenntniss der Atomigkeit der Elemente hervorgegangen sind"; and a little further on:—"Diese beiden Abhandlungen von Kekulé und Couper bilden die Grundlagen unserer Anschauungen über den Aufbau der Verbindungen."

Hermann Kopp, in his work, *Die Entwickelung der Chemie in der neueren Zeit*, gives a similar decision as to Couper's formulæ:—"Die Formeln, durch welche Couper seine hierauf bezüglichen Vorstellungen ausdrückte:—



$$C\left\{\begin{array}{l} O-OH \\ H^3 \end{array}\right.$$

z.B., für den Methyl—,



$$\begin{array}{l} C\left\{\begin{array}{l} O-OH \\ H^2 \end{array}\right. \\ | \\ C-H_3 \end{array}$$

für den Aethylalkohol,

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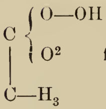
* Compare also Ernst von Meyer's *Geschichte der Chemie*, Leipzig, 1889, S. 270, Anm. 3.

† *Liebig's Annalen*, cxlvi. 260 (Heft ii., issued on 6th May 1868).

‡ S. 269.



$$\begin{array}{l} C\left\{\begin{array}{l} O-OH \\ O^2 \end{array}\right. \\ | \\ C-H_3 \end{array}$$

fur die Essigsäure, u.s.w. :

sie waren bereits solche, wie sie als s.g. Structurformeln weiter zu entwickeln und fester zu begründen viele Chemiker nachher als eine der ihrer Wissenschaft vorzugsweise gestellten Aufgaben betrachteten, viele jetzt es thun." *

I close this section with an extract from Ernst von Meyer's *Geschichte der Chemie von den ältesten Zeiten bis zur Gegenwart,* first published in 1889:—"Ferner legte Couper grossen Nachdruck auf die Fähigkeit der Kohlenstoffatome sich unter einander zu vereinigen und zwar so, dass ein Theil des ihnen eigenen Bindungsvermögens ausgeglichen wird. Diese Vereinigung von Atomen versinnlichte er durch Striche, welche zwischen den mit einander verbundenen Theilchen in den chemischen Symbolen angebracht wurden, er legte so den Grund zu den sogenannten Structurformeln." †

COUPER'S INVESTIGATIONS ON SALICYLIC ACID.

Couper's second and last experimental investigation was laid before the French Academy of Sciences at the meeting of the 7th June 1858. ‡ It was entitled "Recherches sur l'acide salicylique." He says that he undertook this work in order to throw some light on the disputed questions as to the constitution and basicity of salicylic acid. This subject had engaged Chiozza, who worked at it in Gerhardt's laboratory, Gerhardt himself, and his pupil Drion. Unknown to Couper, Kekulé and also Kolbe, along with Lautemann, were at the same time occupied with it. Following these investigations, which had then for their aim the clearing up of the question of the constitution of salicylic acid, we see Gerhardt, Kekulé, Kolbe, and Couper writing formulæ for salicylic acid, and we shall have no difficulty in deciding which of these four investigators made the boldest and most successful advance in this region.

In 1852 Chiozza, probably on the suggestion of Gerhardt, examined the action of phosphorus pentachloride on gaultheria oil, § at that time the usual source of salicylic acid. He found that, on the distillation of the product of the reaction, a liquid was obtained which behaved like an acichloride, giving chlorobenzoic acid on treatment with water.

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* Page 829.

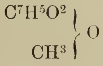
† Page 270.

‡ *Comptes rendus*, xlvi. 1107–1110.

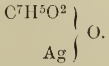
§ *Ibid.*, xxxiv. 850–851, séance du lundi, 31 May 1852.

A succeeding paper by Gerhardt * introduces us to the problem as it presented itself to chemists at that time, eleven years before the foundation of Kekulé's benzene theory. Gerhardt found two anomalies in the behaviour of the ethers of salicylic acid. First, that they give well-defined salts when treated with bases. Second, that treatment with chlorine or bromine does not lead to substitution in the alcohol radicals, but to the formation of ethers of chloro- or bromo-salicylic acid.

At first Gerhardt gave "salicylate de méthyle (huile de gaultheria)" a formula similar to that of silver salicylate:—

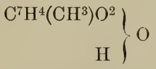


$$\left.\begin{array}{r} C^7H^5O^2 \\ CH^3 \end{array}\right\} O$$



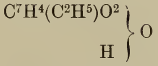
$$\left.\begin{array}{r} C^7H^5O^2 \\ Ag \end{array}\right\} O.$$

The first of the two anomalies—the only one that interests us here—led Gerhardt to regard the ethers of salicylic acid not "comme une molécule d'eau dont 2 atomes d'hydrogène étaient remplacés l'un par du salicyle et l'autre par du méthyle ou d'éthyle," but "comme une molécule d'eau dont 1 atome d'hydrogène seulement était remplacé par le groupe méthylsalicyle ou éthylsalicyle, c'est-à-dire par du salicyle contenant déjà lui-même du méthyle ou de l'éthyle en substitution à de l'hydrogène:—



$$\left.\begin{array}{r} C^7H^4(CH^3)O^2 \\ H \end{array}\right\} O$$

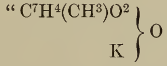
Hydrate de méthylsalicyle.



$$\left.\begin{array}{r} C^7H^4(C^2H^5)O^2 \\ H \end{array}\right\} O$$

Hydrate d'éthylsalicyle."

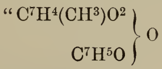
Correspondingly, he gives the potash salt of gaultheria oil the formula and name:—



"$$\left.\begin{array}{r} C^7H^4(CH^3)O^2 \\ K \end{array}\right\} O$$

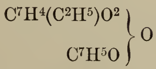
Oxyde de potasse et méthylsalicyle."

He adds:—"L'expérience a pleinement justifié mes présomptions. Rien n'est plus facile, en effet, que d'éthérifier les éthers salicyliques, comme on éthérifie l'alcool ou l'esprit-de-bois." For, by treatment with benzoyl chloride, the salicylic ethers give the corresponding benzoyl derivatives.



"$$\left.\begin{array}{r} C^7H^4(CH^3)O^2 \\ C^7H^5O \end{array}\right\} O$$

Benzoate de méthylsalicyle, ou oxyde de benzoïle et de méthylsalicyle.



$$\left.\begin{array}{r} C^7H^4(C^2H^5)O^2 \\ C^7H^5O \end{array}\right\} O$$

Benzoate d'éthylsalicyle ou oxyde de benzoïle et d'éthylsalicyle."

In order to obtain the "chlorure de méthylsalicyle," Gerhardt sub-

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* *Comptes rendus*, xxxviii. 32–34, séance du lundi, 9 Jan. 1854.

jected gaultheria oil to the action of phosphorus pentachloride; but, to his surprise, he obtained, after a vigorous action, both from the methyl and from the ethyl ether, a new chloride, "chlorure de salicyle," $\left.\begin{matrix}C^7H^5O^2\\ Cl\end{matrix}\right\}$. It is obvious that Gerhardt did not distil the product as Chiozza had done, but drew his conclusion as to its nature only from the action on it of methyl and ethyl alcohol, by which it is retransformed into ethers of salicylic acid. Gerhardt does not quote Chiozza's paper, nor does he discuss its contents.

Gerhardt's pupil, Drion, further extended Gerhardt's experiments on salicylic ethers.* His observations are of interest to us here, as he describes the preparation of salicyl chloride somewhat more in detail than Gerhardt had done:—"Le *chlorure de salicyle* que j'emploie pour la préparation du salicylate d'amyle a été obtenu, pour la première fois, par M. Gerhardt, en faisant agir le perchlorure de phosphore sur l'huile de gaulthéria. Dans cette réaction remarquable, il ne se forme que des traces d'oxychlorure de phosphore; mais il se dégage beaucoup d'acide chlorhydrique, et j'ai constaté également la production abondante de chlorure de méthyle. Le chlorure de salicyle peut être chauffé jusque vers 200 degrés sans se décomposer, mais on ne peut le distiller.

"Dans le but de l'obtenir pur j'ai cherché à le distiller sous une pression moindre que celle de l'atmosphère. Bientôt d'abondantes fumées d'acide chlorhydrique sont sorties de la pompe et m'ont contraint de renoncer à l'emploi de cet appareil. J'ai continué la distillation sous la pression atmosphérique, et j'ai recueilli dans le récipient un liquide fumant, présentant tous les caractères des chlorures organiques."

Treated with water, the distillate yielded a mixture of salicylic and chlorobenzoic acids, from which Drion concluded that the "chlorure de chlorobenzoïle, C^7H^4ClO, Cl," was formed by the decomposition of the "chlorure de salicyle." "Il avait été obtenu déjà par M. Chiozza en faisant agir le perchlorure de phosphore sur l'acide salicylique."

I sum up the collection of observations made in Gerhardt's laboratory by Chiozza, Gerhardt, and Drion on the action of phosphorus pentachloride on gaultheria oil. The violent reaction of the two substances takes place with the evolution of hydrochloric acid and methyl chloride: only traces of phosphorus oxychloride are produced. The undistilled product of the reaction, when treated with methyl alcohol, gives methyl salicylate, and was therefore pronounced to be salicyl chloride, the acichloride of salicylic acid. But the supposed salicyl chloride cannot be distilled unchanged, either under ordinary or under reduced pressure. The product obtained by distilling under ordinary pressure gives, with water, salicylic acid and monochlorobenzoic acid, and was therefore regarded as a mixture of the acichlorides of these acids.

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* *Comptes rendus*, xxxix. 122–125, séance du lundi, 10 juillet 1854.

The puzzling thing was, what had become of the phosphorus oxychloride which must have been formed by the reaction of the hydroxyl of the salicylic acid with the phosphorus pentachloride? The production of chlorbenzoyl chloride from the supposed salicyl chloride was also unintelligible. Besides, most of the conclusions lacked the support of analysis.

The problem had, therefore, attractiveness enough to lead a sharp-sighted investigator like Couper to attack it again.

I use, for reference in the meantime, only Couper's first paper, that in the *Comptes rendus*,* in which he contented himself with the use of empirical molecular formulæ, as we should now call them, using the atomic weights C = 6 and O = 8. He describes his method and the course of the reaction thus:—He added gaultheria oil in small quantities at a time to the phosphorus pentachloride, in the proportion of one equivalent of the former to two of the latter. After the reaction (which ran exactly the same course when salicylic acid was used) was finished, he distilled the product under ordinary pressure. When the trace of phosphorus oxychloride and the excess of the pentachloride had been driven off, there passed over, between 285° and 295°, a colourless liquid, which he named "*trichlorophosphate de salicyle*, $C^{14}H^4Cl^3PhO^6$," formed according to the equations:

$$\underbrace{C^{16}H^8O^6}_{\text{gaultheria oil}} + PhCl^5 = HCl + C^2H^3Cl + C^{14}H^4Cl^3PhO^6;$$

$$\underbrace{C^{14}H^6O^6}_{\text{salicylic acid}} + PhCl^5 = 2HCl + C^{14}H^4Cl^3PhO^6."$$

The "trichlorophosphate de salicyle" is instantly decomposed by hot water, giving hydrochloric, phosphoric, and salicylic acids; according to the equation:

$$C^{14}H^4Cl^3PhO^6 + 8HO = PhH^3O^8 + 3HCl + C^{14}H^6O^6.$$

If the "trichlorophosphate de salicyle" is quickly distilled, it partially decomposes with abundant evolution of hydrochloric acid. Above 300° there passes over a liquid which, when sealed up in a glass tube, deposits large crystals of "monochlorophosphate de salicyle, $C^{14}H^4O^8ClPh$." Both the trichlorophosphate and the monochlorophosphate take up moisture from the air and give rise to a new acid, "acide phosphosalicylique, $C^{14}H^7PhO^{12}$." This is formed in accordance with the equations:

$$C^{14}H^4Cl^3PhO^6 + 6HO = 3HCl + C^{14}H^7PhO^{12};$$

$$C^{14}H^4ClPHO^8 + 4HO = HCl + C^{14}H^7PhO^{12}.$$

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* xlvi. 1107–1110.

The "acide phosphosalicylique" is tribasic, and Couper regarded it "comme une combinaison conjugée d'acide phosphorique et d'acide salicylique,

$$PhH^3O^8 + C^{14}H^6O^6 = C^{14}H^7PhO^{12} + 2HO."$$

These results, says Couper, do not, in all points, agree with the observations published by Gerhardt, Chiozza, and Drion, and raise a doubt as to the existence of the salicyl chloride described by Gerhardt, a product that has never been analysed. Couper then points out that the formation of salicyl chloride from salicylic acid or from gaultheria oil could not take place without the production of phosphorus oxychloride, whereas he had observed only traces of this substance. Whether these contradictions were the result of some accident or of special conditions under which the various observers worked, could only be decided by new investigations.

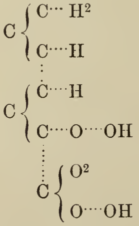
The formulæ of the three new compounds containing phosphorus, which he had obtained from salicylic acid, were substantiated by Couper by means of a series of analyses. He used empirical molecular formulæ and the small equivalent weights $C = 6$ and $O = 8$.

A week after the publication of this paper on salicylic acid, there appeared, in the *Comptes rendus*, Couper's first communication on a new chemical theory. He applies his new theory to the derivation of constitutional formulæ for salicylic acid and for his "trichlorophosphate de salicyle," assuming $C = 12$, but retaining $O = 8$.

In the somewhat later paper, published in the *Edinburgh New Philosophical Journal*, he gives constitutional formulæ, not only for these, but also for the "monochlorophosphate de salicyle" and the "acide phosphosalicylique." These formulæ are given below as I_a, II_a, III_a, and IV_a, and beside them I have given, as I_b, II_b, III_b, and IV_b, the formulæ obtained by doubling the atomic weight of oxygen:

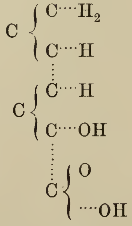
Salicylic Acid.

I_a.



$$\begin{array}{l} C\left\{\begin{array}{l}C\cdots H^2\\ C\cdots H\end{array}\right.\\ \quad\vdots\\ C\left\{\begin{array}{l}C\cdots H\\ C\cdots O\cdots OH\end{array}\right.\\ \quad\vdots\\ \quad C\left\{\begin{array}{l}O^2\\ O\cdots OH\end{array}\right.\end{array}$$

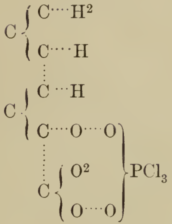
I_b $(O = 16)$.



$$\begin{array}{l} C\left\{\begin{array}{l}C\cdots H_2\\ C\cdots H\end{array}\right.\\ \quad\vdots\\ C\left\{\begin{array}{l}C\cdots H\\ C\cdots OH\end{array}\right.\\ \quad\vdots\\ \quad C\left\{\begin{array}{l}O\\ \cdots OH\end{array}\right.\end{array}$$

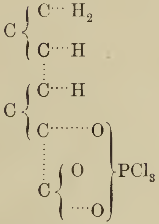
From this formula ($\mathrm{I}_{\bar{a}}$) for salicylic acid Couper derives the following formula for the "terchlorophosphate of salicyle":—

II_a.



$$\begin{array}{l}\mathrm{C}\left\{\begin{array}{l}\mathrm{C\cdots H^2}\\\mathrm{C\cdots H}\end{array}\right.\\\vdots\\\left.\begin{array}{l}\mathrm{C}\left\{\begin{array}{l}\mathrm{C\cdots H}\\\mathrm{C\cdots O\cdots O}\end{array}\right.\\\vdots\\\mathrm{C}\left\{\begin{array}{l}\mathrm{O^2}\\\mathrm{O\cdots O}\end{array}\right.\end{array}\right\}\mathrm{PCl_3}\end{array}$$

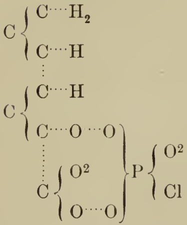
$\mathrm{II}_b\ (\mathrm{O}=16)$.



$$\begin{array}{l}\mathrm{C}\left\{\begin{array}{l}\mathrm{C\cdots H_2}\\\mathrm{C\cdots H}\end{array}\right.\\\vdots\\\left.\begin{array}{l}\mathrm{C}\left\{\begin{array}{l}\mathrm{C\cdots H}\\\mathrm{C\cdots\cdots O}\end{array}\right.\\\vdots\\\mathrm{C}\left\{\begin{array}{l}\mathrm{O}\\\mathrm{\cdots O}\end{array}\right.\end{array}\right\}\mathrm{PCl_3}\end{array}$$

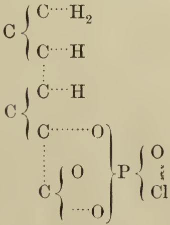
Monochlorophosphate of Salicyle.

III_a.



$$\begin{array}{l}\mathrm{C}\left\{\begin{array}{l}\mathrm{C\cdots H_2}\\\mathrm{C\cdots H}\end{array}\right.\\\vdots\\\left.\begin{array}{l}\mathrm{C}\left\{\begin{array}{l}\mathrm{C\cdots H}\\\mathrm{C\cdots O\cdots O}\end{array}\right.\\\vdots\\\mathrm{C}\left\{\begin{array}{l}\mathrm{O^2}\\\mathrm{O\cdots O}\end{array}\right.\end{array}\right\}\mathrm{P}\left\{\begin{array}{l}\mathrm{O^2}\\\mathrm{Cl}\end{array}\right.\end{array}$$

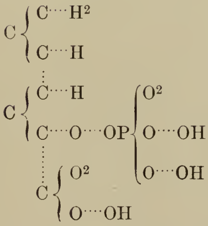
$\mathrm{III}_b\ (\mathrm{O}=16)$.



$$\begin{array}{l}\mathrm{C}\left\{\begin{array}{l}\mathrm{C\cdots H_2}\\\mathrm{C\cdots H}\end{array}\right.\\\vdots\\\left.\begin{array}{l}\mathrm{C}\left\{\begin{array}{l}\mathrm{C\cdots H}\\\mathrm{C\cdots\cdots O}\end{array}\right.\\\vdots\\\mathrm{C}\left\{\begin{array}{l}\mathrm{O}\\\mathrm{\cdots O}\end{array}\right.\end{array}\right\}\mathrm{P}\left\{\begin{array}{l}\mathrm{O}\\\mathrm{Cl}\end{array}\right.\end{array}$$

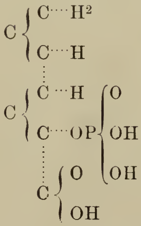
Phosphosalicylic Acid.

IV_a.



$$\begin{array}{l}\mathrm{C}\left\{\begin{array}{l}\mathrm{C\cdots H^2}\\\mathrm{C\cdots H}\end{array}\right.\\\vdots\\\mathrm{C}\left\{\begin{array}{l}\mathrm{C\cdots H}\\\mathrm{C\cdots O\cdots OP}\left\{\begin{array}{l}\mathrm{O^2}\\\mathrm{O\cdots OH}\\\mathrm{O\cdots OH}\end{array}\right.\end{array}\right.\\\vdots\\\mathrm{C}\left\{\begin{array}{l}\mathrm{O^2}\\\mathrm{O\cdots OH}\end{array}\right.\end{array}$$

$\mathrm{IV}_b\ (\mathrm{O}=16)$.



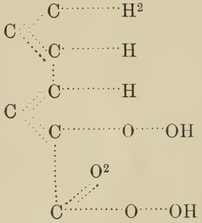
$$\begin{array}{l}\mathrm{C}\left\{\begin{array}{l}\mathrm{C\cdots H^2}\\\mathrm{C\cdots H}\end{array}\right.\\\vdots\\\mathrm{C}\left\{\begin{array}{l}\mathrm{C\cdots H}\\\mathrm{C\cdots OP}\left\{\begin{array}{l}\mathrm{O}\\\mathrm{OH}\\\mathrm{OH}\end{array}\right.\end{array}\right.\\\vdots\\\mathrm{C}\left\{\begin{array}{l}\mathrm{O}\\\mathrm{OH}\end{array}\right.\end{array}$$

These formulæ, I_a, II_a, III_a, and IV_a, are structural formulæ, in our present meaning of the term. They strike us as still more modern when, in them, we use $\mathrm{O}=16$, that is, divide the number of oxygen atoms by 2 (or write O for Couper's O^2 or $-\mathrm{O}-\mathrm{O}-$), as is shown in the formulæ I_b, II_b, III_b, IV_b. The formulæ II_a and II_b show us what has become of the phosphorus pentachloride, the residue of which replaces the hydrogen of the hydroxyl and of the carboxyl in the salicylic acid. We see that Couper supposed the hydroxyl and the carboxyl to be attached to the same carbon atom.

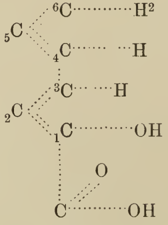
Thus, so early as seven years before the establishment of Kekulé's benzene theory, Couper endeavoured to take account of the mode of union of the seven carbon atoms of salicylic acid.

As I have pointed out in the preceding section, Couper, in his fuller paper in the *Philosophical Magazine*, "On a New Chemical Theory," everywhere replaces the brackets of his structural formulæ by lines indicating the union of the atoms. If we carry this out in the case of the eight formulæ given above, and represent, as has been done in later times, the double union by two parallel lines, we obtain the following eight forms, I_c, II_c, III_c, IV_c, and I_d, II_d, III_d, IV_d:—

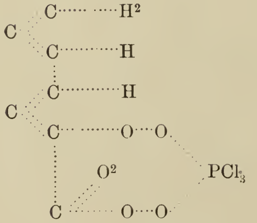
I_c.



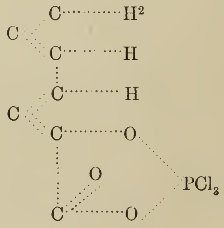
I_d (O = 16).



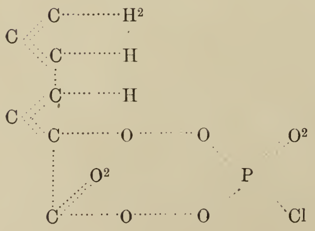
II_c.



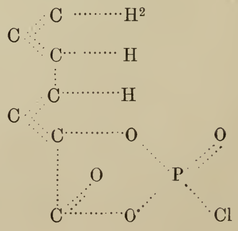
II_d (O = 16).



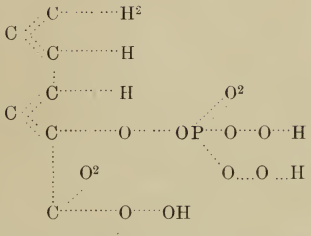
III_c.



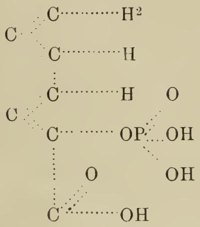
III_d (O = 16).



IV_c.



IV_d (O=16).



As I said some time ago, in discussing these formulæ *:—"If my reconstruction of Couper's formulæ is justifiable, these formulæ clearly show what Couper lacked for the discovery of the benzene theory. Four carbon atoms—I have numbered them in formula I_d; they are 2, 3, 4, and 5—are represented by Couper in the same state of combination with one another as Kekulé's formula gave them at a later date." Couper had only to take one step more, to unite the carbon atoms 6 and 1, and close the ring: this would have involved the transference of a hydrogen atom from 6 to 5, and of the hydroxyl from 1 to 2. And Couper had already arrived at the assumption of the union of multivalent atoms in ring form, as is shown by the formula, given in an earlier part of this paper (p. 216, and Appendix, p. 265), by which Couper expressed the constitution of cyanuric acid. "Undoubtedly Archibald Couper was, at that time, August Kekulé's most dangerous rival."

Of the three chemists whose work was criticised in Couper's salicylic acid paper, Gerhardt was gone (having died August 19, 1856, in Strassburg, soon after his settlement there), Chiozza said nothing, and only Drion attempted to defend himself and Gerhardt.† He maintained that the existence of the salicyl chloride observed by Gerhardt, although not isolated in a pure state owing to its nonvolatility, was indubitably proved by the readiness with which it reproduced the ethers of salicylic acid when treated with alcohols. It will be seen that Drion makes his task too easy: he tries neither to refute Couper's description of the course of the reaction nor to explain what became of the phosphorus oxychloride, which must have been produced in the formation of salicyl chloride, but which neither he nor Couper had observed.

It is remarkable that Couper and Kekulé encountered one another not only in the theoretical but also in the experimental field. Kekulé, in

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* *Liebig's Annalen*, cccxlvi. 290.

† *Comptes rendus*, xlvi. 1238, séance du lundi, 21 juin 1858.

connection with the formation of glycollic acid from monochloracetic acid, tried to convert monochlorobenzoic acid into salicylic acid. He prepared the chlorobenzoic acid from its chloride, which he obtained, according to Chiozza's directions, by distilling the product of the reaction of phosphorus pentachloride on salicylic acid. His attempts to pass from the sodium salt of chlorobenzoic acid to salicylic acid, as he * and Reinhold Hoffmann † had obtained glycollic acid from chloracetic acid, convinced Kekulé of the small reactive power of the chlorine in chlorobenzoic acid. He could as little replace it by hydroxyl as Couper could the bromine in brombenzene and dibrombenzene. This communication of Kekulé, "Bildung von Glykolsäure aus Essigsäure," which closes with the experiments as to salicylic acid, was sent to the editors of *Liebig's Annalen* on the 25th December 1857. Couper's paper on salicylic acid appeared in the first June number of the *Comptes rendus*,‡ so that Kekulé could not have known anything of this work of Couper. But, after the appearance of Couper's paper, Kekulé, who had in the meantime moved from Heidelberg to Ghent, applied himself with the greatest zeal to the continuation of his work on salicylic acid. In his communication laid before the Belgian Academy on the 4th August 1860,§ entitled, "Faits pour compléter l'histoire de l'acide salicylique et de l'acide benzoique," which appeared in the number of *Liebig's Annalen* || published 4th February 1861, under the title, "Beiträge zur Kenntniss der Salicylsäure und der Benzoesäure," Kekulé minutely discusses Couper's work.

Kekulé gives salicylic acid the formula

$$\left.\begin{array}{r}\overset{''}{\text{Ȼ}_7\text{H}_4\Theta}\\ \text{H}_2\end{array}\right\}\Theta_2$$

The phosphorus compound, $C^7H^4Cl^3PO^3$, described by Couper, is regarded by Kekulé as an indirect combination of phosphorus oxychloride with the anhydride of salicylic acid, or as a compound of the radicals salicyl and phosphoryl, belonging to a mixed type, according to the formula

$$\left.\begin{array}{r}\overset{''}{\text{Ȼ}_7\text{H}_4\Theta}\\ \overset{'''}{\text{P}\Theta}\end{array}\right\}\begin{array}{l}\text{Cl}_3\\ \Theta\end{array};\ \text{type}\ \begin{array}{l}\text{H}_3\text{Cl}_3\\ \text{H}_2\text{O}\end{array}=\text{H}_2\text{O}+3\text{HCl}.$$

He cannot confirm Couper's statements as to the products of the action of phosphorus pentachloride on salicylic acid or on its methyl ether. He writes, in the *Annalen*:—"Ich habe diesen Versuch mehr als 20mal

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* *Liebig's Annalen*, cv. 286–292 (Heft iii. issued 27th Maerz 1858).

† *Ibid.*, cii. 12.

‡ xlvi. 1107–1110.

§ *Bull. Acad. Roy. Belg.* (2), x. 337–350.

|| cxvii. 145–164.

wiederholt und dabei mehrmals beträchtliche Mengen der Materialien und in sehr wechselnden Mengen in Arbeit genommen. Ich habe niemals den von Couper beschriebenen Körper erhalten, der nach diesem Chemiker bei 285° bis 295° überdestilliert. Ich habe vielmehr stets beobachtet, dass, sobald die Temperatur der überdestillierenden Dämpfe auf höchstens 280° gestiegen ist, der Rückstand in der Retorte sich unter heftigem Aufblähen und mit Hinterlassung einer schwarzen blasigen Masse zersetzt. Ich habe mich ausserdem überzeugt, dass 1 Molecül Methylsalicylsäure" [that is, gaultheria oil, the methyl ether of salicylic acid] "nur 1 Molecül Phosphorsuperchlorid zu zersetzen im Stande ist, und dass alles im Überschuss zugesetzte Phosphorsuperchlorid bei der ersten Destillation unverändert überdestilliert. Ich habe ferner gefunden, im Widerspruch mit den Angaben von Couper dass eine sehr beträchtliche Menge von Phosphoroxychlorid gebildet wird." "Ich habe endlich gefunden, das der Rückstand in der Retorte, man mag die Destillation zu Ende führen oder in irgend einer Periode unterbrechen, bei Zersetzung mit Wasser oder Kali wessentlich Salicylsaüre liefert, die nur Spuren von Chlorbenzoesaüre enthält."

The key to Kekulé's want of success is to be found in the fact that he had kept the product of the reaction too long at a temperature of 180°–200°, to expel the phosphorus oxychloride and the excess of phosphorus pentachloride, before proceeding to distil, so that he obtained chlorbenzoyl chloride. This is shown with a probability bordering on certainty by the fact that Kekulé found, in the undistilled chloride, only 3 per cent. of phosphorus,* while Couper's "trichlorophosphate de salicyle" contains 11·5 per cent.

As Kekulé was induced by his researches on glycollic acid to occupy himself with salicylic acid, so Hermann Kolbe was led to salicylic acid from the transformation of lactic acid into chloropropionic acid. His work, in which he was seconded by E. Lautemann, appeared under the title, "Über die Constitution und Basicität der Salicylsäure," in the number of *Liebig's Annalen*,† issued 11th August, 1860. Kekulé's communication on salicylic and benzoic acids was presented to the Belgian Academy on the 4th of August of the same year, so that it was only in the German version of his paper in the number of the *Annalen* issued 4th February 1861, that he could take notice of Kolbe and Lautemann's work; but Kekulé's remarks in opposition to Kolbe have no reference to the action of phosphorus pentachloride on salicylic acid, and therefore need not be referred to here.

Kolbe and Lautemann make no reference to Couper's salicylic acid paper, which, indeed, they do not seem to have seen. They prepared the chloride of chlorobenzoic acid (called by them chlorosalylic acid) by Chiozza's * method, as follows:—" Wir brachten in eine tubulierte Retorte 3 Theile (2 Aeq.) gepulverten Fünffach Chlorphosphor, den wir durch längeres Eintauchen des Retortenbauchs in Eiswasser stark erkälteten, und hierauf 1 Theil (1 Aeq.) trockene pulverige Salicylsäure. Beide wurden durch Umschütteln oder durch Umrühren mit einem krummen Glasstab gut gemischt.

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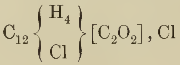
* Compare *Liebig's Annalen*, cxvii. 148, Anm.

† *Ibid.*, cxv. 157–206.

" Alsbald erfolgt eine heftige Reaction, wobei der Inhalt der Retorte sich unter Aufblähen verflüssigt und Salzsäure in Strömen entweicht. Bei nachherigem Erhitzen geht der grösste Theil der flüssigen Masse als farbloses Liquidum über. Der Rest bläht sich zuletzt stark auf und es hinterbleibt schliesslich eine leichte schwammige Kohle. Bei der Rectification des Destillates geht zuerst Phosphoroxychlorid über, hernach steigt die Siedetemperatur ziemlich rasch bis 260° C. Als das Thermometer 240° C. anzeigte wurde die Vorlage gewechselt. Der grösste Theil der noch übrigen Flüssigkeit geht dann zwischen 260° und 270° C. über, erst ganz zuletzt steigt die Temperatur noch bis auf 300° C. Was über 240° C. abdestilliert, besteht hauptsächlich aus

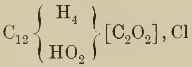
Chlorsalylsäurechlorid.



$$C_{12}\left\{\begin{matrix}H_4\\ Cl\end{matrix}\right\}[C_2O_2], Cl$$

enthält aber daneben noch

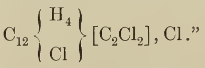
Salicylsaürechlorid.



$$C_{12}\left\{\begin{matrix}H_4\\ HO_2\end{matrix}\right\}[C_2O_2], Cl$$

wie die Bildung von Salicylsäure beim Zusammenbringen mit Wasser beweist, und ausserdem

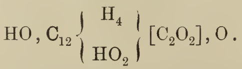
Chlorsalyltrichlorid.



$$C_{12}\left\{\begin{matrix}H_4\\ Cl\end{matrix}\right\}[C_2Cl_2], Cl."$$

Kolbe wrote, for salicylic acid itself, the following formula:—

Salicylic Acid.



$$HO, C_{12}\left\{\begin{matrix}H_4\\ HO_2\end{matrix}\right\}[C_2O_2], O.$$

Obviously, Kolbe and Lautemann, in the distillation of the product of

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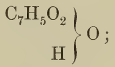
* *Annales de chim. et de phys.* (1852) [3], xxxvi. 102–107.

the reaction, had obtained in the distillate some of Couper's "trichlorophosphate de salicyle," which had passed over undecomposed. But they regarded it as a mixture of salicyl chloride and chlorosalyl chloride, because with water they obtained salicylic and chlorosalylic (chlorobenzoic) acids. They did not test the distillate for phosphorus, and took no note of the possibility of the formation of a derivative of salicylic acid containing phosphorus.

I now place together the formulæ assigned to salicylic acid by Gerhardt, by Couper, by Kekulé, and by Kolbe, appending to Couper's formula (I_a, p. 224 of this paper) the formula I have deduced from it by putting O = 16, and replacing the brackets by lines representing bonds (I_d, p. 226).

Salicylic Acid:

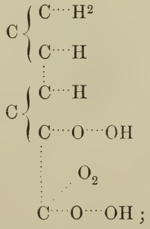
according to Gerhardt:



$$\left.\begin{array}{r}\mathrm{C_7H_5O_2}\\ \mathrm{H}\end{array}\right\}\mathrm{O};$$

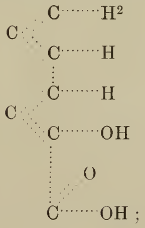
according to Couper:

I_a.

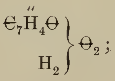


reconstructed with O = 16, and lines in place of brackets:

I_d.

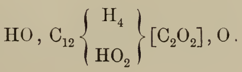


according to Kekulé:



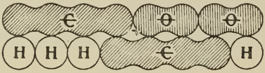
$$\left.\begin{array}{r}\overset{\prime\prime}{\mathrm{C_7H_4\Theta}}\\ \mathrm{H_2}\end{array}\right\}\Theta_2;$$

according to Kolbe:



$$\mathrm{HO},\ \mathrm{C_{12}}\left\{\begin{array}{c}\mathrm{H_4}\\ \mathrm{HO_2}\end{array}\right\}[\mathrm{C_2O_2}],\ \mathrm{O}.$$

Kekulé himself, as will be seen, had not yet, in the year 1860, ventured to express an opinion as to the mode in which the seven atoms of carbon are united to one another, although he had already, in the first part (published in the spring of 1859) of his *Lehrbuch der organischen Chemie*, sought to represent the structure of simple inorganic and organic compounds by means of graphic formulæ, which for lucidity leave nothing to be desired, as, for instance, the formula of acetic acid: *



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Involuntarily the thought arises—how would Archibald Scott Couper have supported his observations and his views in the face of the opposition of his fellow-chemists? Would not organic chemistry have undergone a more rapid development if he had succeeded in fully working out his ideas as to the mode of constructing the formulæ of carbon compounds? Couper was just the man to do that.

But what was this investigator like, who, so young and, after so short an acquaintance with chemistry and at the time of which we are speaking, ventured to pronounce on the mode of union of the atoms in such complicated compounds as salicylic acid, tartaric acid, mucic acid, grape sugar, cyanuric acid, etc.?

Mr Berring gives us from the treasury of his memory the following picture of his friend:—

"Couper was a very handsome man, tall and slender, of a distinguished, aristocratic aspect. His fine face, with its glowing colour, was animated by the almost miraculous brilliancy of his deep black eyes. He had no appearance of weakness, but yet his health was delicate, and I have heard Hamilton say that his mother was always anxious about him. The basis of his character, as is often the case with Scotsmen, was deeply religious. He was very fond of music—classical, serious, and lively—and seldom missed a good concert when he was in Berlin."

Mr Berring wrote to Crum Brown, on receiving from him a copy of the portrait prefixed to this biography: "This is an excellent picture, and will let you see that Couper was the strikingly handsome man I described." The original of the portrait is a hand-coloured photograph in the possession of Mr Dollar. It was taken in Paris in 1857, or in the beginning of 1858, and is therefore of the same date as Couper's scientific work. Couper's features betray an energetic will combined with a penetrating understanding. In his theoretic paper, his pleasure in the philosophical, critical treatment of the fundamental principles of chemistry is unmistakable. His mode of thought is quite his own, his statements of his observations, supported by excellent analyses, are clear and definite.

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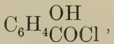
* Compare Bd. i., Seite 164, Anm.

Is it not strange that such an investigator should have made no answer to the criticisms of his theoretical views by Kekulé, Wurtz, and Butlerow; that he made no attempt to refute the doubts of Drion and of Kekulé as to the accuracy of his work on salicylic acid? But no further writing came from Couper's pen. As a scientific man he had disappeared, and twenty-seven years had to elapse before the correctness of his statements as to the action of pentachloride of phosphorus on salicylic acid was demonstrated by another.

In the meantime, quite a number of chemists had busied themselves with the supposed salicyl chloride, mostly in order to study its action on other substances. Carius,* with the view of obtaining thiosalicylic acid, brought the undistilled product of the action of phosphorous pentachloride on salicylic acid into reaction with an aqueous solution of excess of potassium sulphide. In Kolbe's laboratory Glutz,† in 1867, showed that, by continued heating with a reflux condenser, for a day, of gaultheria oil with two equivalents of phosphorus pentachloride, the latter ultimately completely disappears, and a better yield of chlorsalyl chloride is obtained. He states that, on distilling, after the phosphorus oxychloride has been driven off, the temperature quickly rises to 230°–260°, and that below 240° the distillate consists half of chlorsalyl chloride and half of salicyl chloride.

Pierre Miquel ‡ prepared "salicyl carbimide" by the action of undistilled "salicyl chloride" on metallic thiocyanates, and remarks: "Le chlorure de salicyle s'obtient difficilement dans un état de pureté satisfaisant, il renferme toujours des composés visqueux et retient avec beaucoup d'énergie de l'oxychlorure de phosphore."

Otto Fischer, § in the same year, by heating "the chloride  $C_6H_4\genfrac{}{}{0pt}{}{OH}{COCl}$, freed as much as possible from phosphorus compounds," to 180° with dimethyl aniline and zinc dust in a current of carbonic anhydride, obtained the saliceïn of dimethyl aniline.

Schreib, ‖ in 1880, states that in the action of phosphorus pentachloride on salicylic acid only one molecule of the pentachloride enters into reaction; a second molecule is without effect and is recovered unchanged on heating to about 110°. He goes on to say: "Bei weiterem Erhitzen geht zuerst ein grosser Theil des gebildeten Phosphoroxychlorid und später Orthochlorbenzoylchlorid über, bis sich, bei circa 260°–270° der Retorteninhalt unter starkem Aufschäumen zersetzt."

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* *Liebig's Annalen*, cxxix. 11 (Heft i., issued 8th Jan. 1864).

† *Ibid.*, cxliii. 194 (Heft ii., issued 20th July 1867).

‡ *Annales de chim. et de phys.* (1877) [5], xi. 304.

§ *Berl. Ber.* (1877), x. 954.

‖ *Ibid.* (1880), xiii. 465.

From all these statements it will be seen that it is difficult to obtain Couper's "trichlorophosphate de salicyle" from the product of the action of phosphorus pentachloride on salicylic acid by distilling under ordinary pressure. Contrary to Drion's statement, the difficulties disappear, as I showed in the year 1885,* when the distillation is conducted under diminished pressure. By working exactly according to Couper's description, with the materials he used, and distilling quickly, immediately after the reaction is finished, under ordinary pressure, "trichlorophosphate de salicyle" is also obtained, although the yield is not so good. In the course of exhaustive investigations, carried out along with George Dunning Moore, we were able also to confirm Couper's statements as to the "monochlorophosphate de salicyle" and the "acide phosphosalicylique."

And thus, certainly late enough, there came a brilliant justification of Couper's work on salicylic acid, work which chemists had gradually come to look on as so certainly inaccurate that no notice was taken of it in any of the treatises on organic chemistry.

How often since then have I longed to know what became of Couper!

No doubt, there have been cases of English chemists who, after a meteor flash of one brilliant piece of scientific work, taken up by other engagements, have for many years been absent from the purely scientific field; still, they have always attained a position which could not allow their names to be overlooked, not to say to be forgotten. It was otherwise with Archibald Scott Couper. He disappeared so suddenly and so completely from the scientific arena that there was not time for his name to gain entrance into the English, German, or French books of scientific biography.

This enigma was completely solved by the investigations of his countryman, Alexander Crum Brown. It was not his disappointment that, by no fault of his, his paper, "Sur une nouvelle théorie chimique," was not presented to the French Academy of Sciences until after the publication of Kekulé's famous paper, "Über die Constitution und die Metamorphosen der chemischem Verbindungen und die chemische Natur des Kohlenstoffs," that broke Couper down, but a severe attack of illness.

Having returned, late in the autumn of 1858, from France to Scotland, he obtained, in the end of December, the post of second laboratory assistant to the distinguished Professor Lyon Playfair, Edinburgh.

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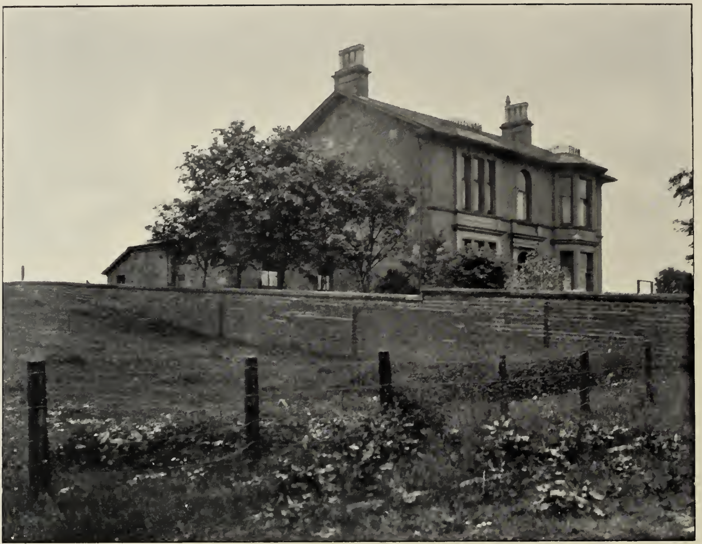
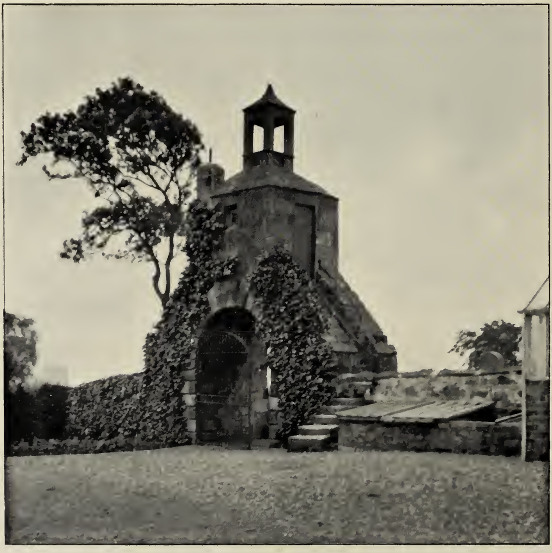
* *Liebig's Annalen*, ccxxviii. 308–321 (Heft. iii., issued 18th May 1885).



Laurel Bank, Kirkintilloch. June 23, 1906.



Entrance to Kirkintilloch Cemetery. June 23, 1906.

His future academic position seemed thus made secure.

But soon after his entry on his new office, Couper suffered from a serious breakdown in health, and for two months was under special medical care. On his recovery he went on a fishing expedition, when over-exertion and long exposure to the sun caused a return of his illness, necessitating retirement and medical treatment for a longer time. Greville Williams was therefore quite right in his recollection of a sunstroke. He never completely recovered, and was incapable of undertaking any serious work, but lived in retirement, tenderly cared for by his mother—at first in the old home in the Townhead, and after 1880 in the comfortable house, Laurel Bank, Kirkintilloch, which she had built specially as a quiet home for him. His father died on the 30th December 1859, in his sixty-second year.

Couper's health seems to have somewhat improved, and he was able to take a long walk every day, to converse occasionally with friends, and now and then write a letter. Every morning and evening he read aloud to the household a chapter of the New Testament, and went regularly to church on Sundays.

He died, unmarried, at Laurel Bank, on the 11th March 1892, almost sixty-one years old.

His mother had the sad satisfaction of nursing him to the end. She died at Laurel Bank, 15th April 1895, at the advanced age of ninety-three.

The house, Laurel Bank, in which Couper lived for twelve years, and where he and his mother died, as also the picturesque entrance gate of the Kirkintilloch cemetery, where he and his ancestors are buried, are shown in the plates taken from photographs by Crum Brown.

In the history of organic chemistry the sorely tried Archibald Scott Couper deserves a place of honour beside his more fortunate fellow-worker, Friedrich August Kekulé.

APPENDIX I.

Recherches sur la benzine; par M. A. Couper.*

Supposant qu'il serait possible de transformer la benzine en alcool et en glycol phényliques, j'ai été conduit à faire avec ce carbure d'hydrogène les expériences suivantes.

Lorsqu'on fait arriver dans un appareil convenable, de la vapeur de brome dans de la benzine bouillante, il se dégage de l'acide bromhydrique, et l'on obtient successivement deux composés bromés, la bromobenzine et la dibromobenzine.

La *bromobenzine* (bromine de phényle), $C^{12}H^5Br$, passe à 150 degrés. C'est

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* *Comptes rendus*, t. xlv. pp. 230–232 (10 aout 1857).

un liquide parfaitement incolore, doué d'une odeur analogue à celle de la benzine elle-même. Il ne se solidifie pas à -20 degrés. Sa densité de vapeur a été trouvée égale à 5,631. La densité de vapeur théorique est de 5,4237. Elle a donné à l'analyse :

	Expérience.	Théorie.
Carbone	45,40	45,86
Hydrogène	3,27	3,18
Brome	50,84	50,94

Elle possède à un degré remarquable la stabilité bien connue de la benzine. Elle réagit à peine sur l'acétate d'argent à la température de 200 degrés. Chauffée avec de l'acide nitrique fumant, elle se transforme en un composé cristallin fusible au-dessous de 90 degrés et volatil sans décomposition.

Ce composé renferme d'après mes analyses $C^{12}H^4(AzO^4)Br$ et se transformerait probablement en bromaniline sous l'influence des agents réducteurs.

La bromobenzine se dissout dans l'acide sulfurique fumant ; la solution abandonnée à l'air laisse déposer, en absorbant l'humidité, des cristaux d'acide sulfobromobenzinique. Cet acide est très-déliquescent. Lorsqu'on ajoute de l'ammoniaque à sa solution aqueuse, il se forme un sel ammoniacal qui est presque insoluble dans l'eau et qui cristallise immédiatement.

Ce sel renferme $C^{12}H^5Br$, S^2O^6, AzH^3, comme le prouvent les analyses suivantes :

	Expérience.	Théorie.
Carbone	27,86	28,34
Hydrogène	3,47	3,14
Brome	31,35	31,48
Azote	5,67	5,51

Lorsqu'on laisse pendant longtemps la monobromobenzine en contact avec un excès de brome, de l'acide bromhydrique se forme et se dégage continuellement, et un corps solide se dépose en cristaux au fond du vase. Ce corps est la *dibromobenzine* qu'on purifie facilement en le faisant cristalliser dans l'éther. La dibromobenzine renferme $C^{12}H^4Br^2$, comme le prouve l'analyse suivante :

	Expérience.	Théorie.
Carbone	30,30	30,50
Hydrogène	1,92	1,69
Brome	...	67,81
		100,00

Elle cristallise en magnifiques prismes obliques.

Elle fond à 89 degrés et distille sans altération à 219 degrés.

Elle réagit sur l'acétate d'argent, mais très-lentement et en formant sans doute du phénylglycol diacétique

$$C^{12}H^4O^2\left\{\begin{matrix}C^4H^3O^3\\C^4H^3O^3\end{matrix}\right. = \left.\begin{matrix}C^{12}H^4\\(C^4H^3O^2)^2\end{matrix}\right\}O^4.$$

Cette expérience ayant été perdue par suite d'une explosion, je me réserve d'en faire le sujet d'une nouvelle étude.

APPENDIX II.

Sur une nouvelle théorie chimique; par M. A. Couper. (Note presentée par M. Dumas.)*

J'ai l'honneur d'exposer à l'Académie les traits principaux d'une nouvelle théorie chimique que je propose pour les combinaisons organiques.

Je remonte aux éléments eux-mêmes dont j'étudie les affinités réciproques. Cette étude suffit, selon moi, à l'explication de toutes les combinaisons chimiques, sans qu'on ait besoin de recourir à des principes inconnus et à des généralisations arbitraires.

Je distingue deux especes d'affinité, savoir:

1°. L'affinité de degré; 2°. l'affinité élective.

J'entends par affinité de degré, l'affinité qu'un élément exerce sur un autre avec lequel il se combine en plusieurs proportions définies. Je nomme affinité élective, celle que différents éléments exercent les uns sur les autres, avec des intensités différentes. Prenant pour exemple le carbone, je trouve qu'il exerce son pouvoir de combinaison en deux degrés. Ces degrés sont représentés par CO^2 et CO^4, c'est-à-dire par l'oxyde de carbone et l'acide carbonique, en adoptant pour les équivalents du carbone et de l'oxygène les nombres 12 et 8.

En ce qui concerne ses affinités électives, le carbone s'éloigne des autres éléments et montre, pour ainsi dire, une physionomie particulière. Les traits qui caractérisent cette affinité élective du carbone sont les suivants:

1°. Il se combine avec des nombres d'équivalents égaux d'hydrogène, de chlore, d'oxygène, de soufre, etc., qui peuvent se remplacer mutuellement pour satisfaire son pouvoir de combinaison.

2°. Il entre en combinaison avec lui-même.

Ces deux propriétés suffisent à mon avis pour expliquer tout ce que la chimie organique offre de caractéristique. Je crois que la seconde est signalée ici pour la première fois. A mon avis, elle rend compte de ce fait important et encore inexpliqué de l'accumulation des molécules de carbone dans les combinaisons organiques. Dans les composés où 2, 3, 4, 5, 6, etc., molécules de carbone sont liées ensemble, c'est le carbone qui sert de lien au carbone.

Ce n'est pas l'hydrogène qui peut lier ensemble les éléments des corps organiques. Si, comme le carbone, il avait le pouvoir de se combiner à lui-même, on devrait pouvoir former les composés H^4Cl^4, H^6Cl^6, H^8Cl^8.

En ce qui concerne l'oxygène, j'admets qu'un atome de ce corps en combinaison exerce une affinité puissante sur un second atome d'oxygène qui lui-même est combiné à un autre élément. Cette affinité est modifiée par la position électrique des éléments auxquels se sont respectivement attachés les atomes d'oxygène. Les développements qui vont suivre feront comprendre cette pensée.

La puissance de combinaison la plus élevée que l'on connaisse pour le carbone est celle du second degré, c'est-à-dire 4.

La puissance de combinaison de l'oxygène est représentée par 2.

Toutes les combinaisons du carbone peuvent être ramenées à deux types. L'un d'eux est représentée par le symbole

$$nCM^4,$$

l'autre par le symbole

$$nCM^4 - mM^2,$$

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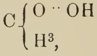
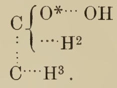
* *Comptes rendus*, t. xlvi. pp. 1157–1160 (14 juin 1858).

où m est $< n$, ou bien $n\mathrm{CM}^4 + m\mathrm{CM}^2$, où n peut devenir nul. On peut citer, comme exemple du premier type, les alcools, les acides gras, les glycols, etc.

Les alcools méthylique et éthylique seront représentés par les formules



$$C\left\{\begin{array}{l} O\cdots OH \\ H^3, \end{array}\right.$$

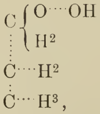


$$\begin{array}{l} C\left\{\begin{array}{l} O^*\cdots OH \\ \cdots H^2 \end{array}\right. \\ \vdots \\ C\cdots H^3. \end{array}$$

On verra facilement que pour l'alcool méthylique la limite de combinaison du carbone est égale à 4, le carbone y étant combiné à 3 d'hydrogène et à 1 d'oxygène. Cet oxygène, dont le pouvoir de combinaison est égal à 2, est à son tour combiné à un autre atome d'oxygène uni lui-même à 1 d'hydrogène.

Dans le cas de l'alcool ordinaire, chacun des deux atomes de carbone satisfait son pouvoir de combinaison d'un côté en s'unissant à 3 atomes d'hydrogène ou d'hydrogène et d'oxygène, et de l'autre côté en s'unissant à l'autre atome de carbone. L'oxygène y est combiné de la même manière que dans l'exemple précédent. Dans ces cas, on verra que le carbone appartient au premier type, chaque atome étant combiné au second degré.

Dans l'alcool propylique,

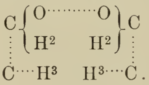


$$\begin{array}{l} C\left\{\begin{array}{l} O\cdots OH \\ H^2 \end{array}\right. \\ \vdots \\ C\cdots H^2 \\ \vdots \\ C\cdots H^3, \end{array}$$

la puissance de combinaison de l'atome de carbone qui est situé au milieu est reduite à 2 pour l'hydrogène, puisqu'il est combiné chimiquement à chacun des deux autres atomes de carbone.

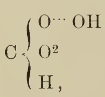
Des formules analogues aux précédentes expriment la constitution des autres alcools.

La constitution de l'éther est représentée par la formule



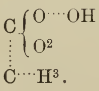
$$\begin{array}{lcr} C\left\{\begin{array}{l} O\cdots\cdots\cdots \\ H^2 \end{array}\right. & & \left.\begin{array}{r} O \\ H^2 \end{array}\right\}C \\ \vdots & & \vdots \\ C\cdots H^3 & & H^3\cdots C. \end{array}$$

L'acide formique est



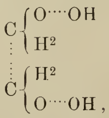
$$C\left\{\begin{array}{l} O\cdots OH \\ O^2 \\ H, \end{array}\right.$$

l'acide acétique



$$\begin{array}{l} C\left\{\begin{array}{l} O\cdots OH \\ O^2 \end{array}\right. \\ \vdots \\ C\cdots H^3. \end{array}$$

La constitution du glycol est représentée par la formule



$$\begin{array}{l} C\left\{\begin{array}{l} O\cdots OH \\ H^2 \end{array}\right. \\ \vdots \\ C\left\{\begin{array}{l} H^2 \\ O\cdots OH, \end{array}\right. \end{array}$$

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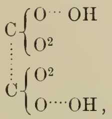
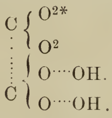
* This "O" is omitted in error in the original.

celle de l'acide oxalique par la formule



$$\begin{array}{l} C\begin{cases} O\cdots OH \\ O^{2} \end{cases} \\ \vdots \\ C\begin{cases} O^{2} \\ O\cdots OH, \end{cases} \end{array}$$

ou, si l'on veut réunir l'oxygène négatif à l'un des pôles de la molécule, par la formule



$$\begin{array}{l} C\begin{cases} O^{2*} \\ O^{2} \end{cases} \\ \vdots \\ C\begin{cases} O\cdots OH. \\ O\cdots OH. \end{cases} \end{array}$$

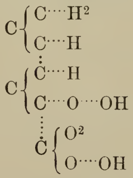
Quoi qu'il en soit cependant, on peut voir d'après cette théorie que, dans la constitution des acides organiques du premier type, la présence de 2 atomes d'oxygène combinés ensemble de manière que tous les deux sont attachés directement au carbone et situés près de l'oxygène négatif, c'est-à-dire de l'oxygène qui entraîne avec lui l'oxygène constitué dans un état électropositif par sa combinaison avec 1 atome d'un élément relativement électropositif, que la présence, dis-je, de ces atomes d'oxygène est nécessaire pour que l'oxygène négatif se trouve dans cet état électrique qui donne au corps les propriétés généralement désignées par le nom d'*acides.*

Ceci est un cas particulier d'une loi générale ; car on peut voir, d'après cette théorie, comment la valeur électropositive ou électronégative des éléments modifie et conditionne mutuellement la valeur électropositive ou électronégative des autres éléments.

Cette loi diffère de l'hypothèse électrique que les chimistes ont défendue autrefois, mais qui n'a jamais pu recevoir une application complète à leurs vues sur la chimie organique ; celle au contraire que j'énonce s'accorde parfaitement avec l'application aux faits de la théorie que je propose.

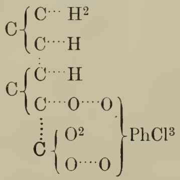
Il ne me reste qu'à ajouter la manière dont je formule l'acide salicylique et le trichlorophosphate de salicyle que j'ai fait connaître dans un travail soumis à l'Académie dans sa dernière séance.

Acide salicylique.



$$\begin{array}{l} C\begin{cases} C\cdots H^{2} \\ C\cdots H \end{cases} \\ \quad\vdots \\ C\begin{cases} C\cdots H \\ C\cdots O\cdots OH \end{cases} \\ \quad\vdots \\ \quad C\begin{cases} O^{2} \\ O\cdots OH \end{cases} \end{array}$$

Trichlorophosphate de salicyle.



$$\begin{array}{l} C\begin{cases} C\cdots H^{2} \\ C\cdots H \end{cases} \\ \quad\vdots \\ C\begin{cases} C\cdots H \\ C\cdots O\cdots O \end{cases} \\ \quad\vdots \\ \quad C\begin{cases} O^{2} \\ O\cdots O \end{cases} \end{array} \Bigg\} PhCl^{3}$$

Ces formules suffisent, pour le moment, pour indiquer mes idées sur la constitution des corps.

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* Misprinted "C^2" for "O^2" in the original.

APPENDIX III *a*.

ON A NEW CHEMICAL THEORY. BY ARCHIBALD S. COUPER, ESQ.
(COMMUNICATED BY THE AUTHOR.*)

The end of chemistry *is its theory.* The guide in chemical research *is a theory.* It is therefore of the greatest importance to ascertain whether the theories at present adopted by chemists are adequate to the explanation of chemical phenomena, or are, at least, based upon the true principles which ought to regulate scientific research.

Among those which have lately been developed, there is one, on account of its apparently numerous merits, which particularly claims investigation, and respecting which we deem that it would not be unprofitable were either new proofs of its scientific value furnished, or, on the contrary, should considerations be adduced establishing not only its inadequacy to the explanation, but its ultimate detriment to the progress of science. I allude to the system of types as advocated by Gerhardt.

This system, striking alike for the breadth of its conception, and the logical and consequent manner in which it has been developed, has been controverted from the point of view afforded by theories less far-reaching than the one under consideration, and even based upon a one-sided and restricted appreciation of certain chemical reactions. The consequence is that this opposition has not impaired the favour with which the unitary system has been received, but has rather tended to display it in a more advantageous light.

Imposing as this theory is, it is nevertheless all the more necessary to submit it to a strict investigation; for there is nothing so prejudicial in the search for truth as the blind spirit of conservation. A rational belief demands the test of a preliminary doubt.

There are two conditions which every sound theory must fulfil :—

1. It must be proved to be empirically true.
2. It must no less be philosophically true.

I admit that this theory is for the most part empirically true; that is to say, it is not contradicted by many of the facts of the science. Evidence that this condition is only partially fulfilled, is to be found—

1. In the circumstance that the peroxides, for instance, do not fit very satisfactorily into the types.

2. The principle of double decomposition cannot well be applied to the conversion of the anhydrous sulphuric acid into the hydrate of that acid by the action of one equivalent of water, the formulæ of these bodies being, according to Gerhardt, in their free state $O.SO^2$ and H^2O. Combined, they become simply SH^2O^4.

The same remark applies in like manner to carbonic acid. In these instances the wonted consequence of Gerhardt is missed. The fact of the density of the vapour of these bodies being the same in the free as in the combined states, may have prevented him from doubling the formulæ of these anhydrous acids. The types of this theory being *essentially types* of double *decomposition*, this instance of a simple

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* *Phil. Mag.*, vol. xvi., 4th series (1858), pp. 104–116.

APPENDIX III *b*.

Sur une nouvelle théorie chimique; par M. A. S. Couper.*

L'étude de la chimie doit avoir pour but l'établissement de la théorie de cette science; une théorie elle-même est un guide qui nous conduit dans les recherches chimiques. Il est donc de la plus grande importance de s'assurer si les théories actuellement admises par les chimistes suffisent pour l'explication des phénomènes chimiques, ou si elles sont au moins basées sur les vrais principes auxquels doivent se soumettre les recherches scientifiques.

Parmi les théories récemment développées, il en est une qui, en raison des nombreux avantages qu'elle paraît offrir, mérite une étude particulièrement approfondie; il nous a semblé d'ailleurs que la science ne pourrait qu'y gagner, soit que cet examen vienne apporter de nouvelles preuves en faveur de cette théorie, soit au contraire qu'il établisse son insuffisance et les dangers qu'elle présente pour les progrès de la science. Je veux parler de la théorie des types, telle qu'elle a été défendue par Gerhardt.

Ce système, remarquable en même temps par la largeur de sa conception et par le développement logique qu'il a reçu, a été combattu au point de vue de théories beaucoup moins satisfaisantes, basées sur une appréciation incomplète de certaines réactions chimiques. Il en est résulté que cette opposition, loin de diminuer la faveur avec laquelle le système unitaire avait été reçu, a plutôt contribué à le montrer sous un jour plus avantageux.

Quelque imposante que soit cette théorie, il n'en est que plus nécessaire de la soumettre à un sévère examen; car rien n'est nuisible, dans la recherche de la vérité, comme l'aveugle attachement aux idées reçues. Une croyance rationelle exige l'épreuve préliminaire du doute.

Toute bonne théorie doit remplir deux conditions:

1°. Il faut qu'elle s'accorde avec l'expérience;

2°. Il n'est pas moins nécessaire qu'elle soit philosophiquement vraie.

J'admets que la théorie unitarienne s'accorde pour la plupart des cas avec l'expérience ou plutôt qu'elle n'est pas contredite par beaucoup des faits de la science.

Cependant les remarques suivantes feront voir que cette condition n'est remplie qu'en partie:

1°. Les peroxydes ne rentrent pas d'une manière bien satisfaisante dans les types;

2°. Le principe de double décomposition ne peut pas bien s'appliquer à la transformation de l'acide sulfurique anhydre en hydrate par l'action de 1 équivalent d'eau: la formule de ces deux corps étant, d'après Gerhardt, à l'état libre, OSO^2 et H^2O, combinés ils deviennent simplement, SH^2O^4.

La même remarque s'applique d'une manière semblable à l'acide carbonique.

Dans l'explication de ces faits, on ne retrouve plus la conséquence habituelle de Gerhardt. La densité de vapeur des acides anhydres de ces corps, étant la même à l'état de liberté et à l'état de combinaison, aurait dû l'empêcher d'en doubler la formule. Les types de Gerhardt étant essentiellement des types de double décom-

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* *Annales de chimie et de physique*, [3], t. liii. (1858), pp. 469–489.

combination diminishes somewhat the value of the otherwise great logical merit of this system.

Having taken notice of such exceptions, the empirical truth of the theory may be otherwise admitted.

The philosophical test demands that a theory be competent to explain the greatest number of facts in the simplest possible manner.

In applying this test, three aspects of it require to be taken into consideration :—

1. As to the extension of the theory.
2. The explanation it affords of the facts.
3. The manner of this explanation.

As to the first: this theory indeed brings every chemical combinate under a certain comparative point of view with every other. Herein apparently is its merit. Nevertheless, should our test be applied to its full extent, it will be found that it is fatal to this system, in other respects so imposing. The comparative point of view which it adopts is fundamentally false.

As to the second: it does not explain the facts at all; consequently the most essential point of the test is unfulfilled.

3. This condition of the test is in like manner unfulfilled from the fact of the second not being complied with.

Why is it that Gerhardt's theory so signally fails in these two essential requisites? Because it is based upon an old but vicious principle, which has already retarded science for centuries. It begins with a generalization, and from this generalization deduces all the particular instances. But it does not come within the limits of a chemical paper to enter upon a discussion which is purely metaphysical. Nevertheless, the theory of Gerhardt can only be combated upon metaphysical grounds, because it is only in overturning a general principle of research that the theory can be proposed. Gerhardt's generalization lacks, moreover, the merit of being represented by a type having a known existence. $n\overset{H}{\underset{H}{O}}$, from which he derives every chemical combinate, being in itself indefinite, cannot of course be contained or be produced in any definite body. That, however, which may be demanded of the type is, that in itself it should afford at least an instance of that which it is meant to represent. Now the part "n" of the type represents the notion of indefinite multiples of $\overset{H}{\underset{H}{O}}$. But not a single instance of a multiple of $\overset{H}{\underset{H}{O}}$ has been proved to exist; much less has it been proved that there exists, or can exist, multiples of this body in an indefinite series. The perfection or imperfection of the type meant to represent the generalized notion is, however, a matter of comparatively inferior moment. It is the principle involved in this generalization which is essentially pernicious.

Should the principle which is therein adopted be applied to the common events of life, it will be found that it is simply absurd. Suppose that some one were to

position, cet exemple de simple combinaison directe diminue en quelque degré la valeur logique de cette théorie, qui est d'ailleurs si grande.

Cette exception une fois constatée, on peut admettre pour le reste la vérité empirique du système.

Il reste à examiner si elle remplit la condition non moins importante de ne pas se trouver en désaccord avec les principes philosophiques.

Ces principes demandent que la théorie puisse expliquer le plus grande nombre possible de faits, de la manière la plus simple.

En soumettant une théorie à cette épreuve, il faut examiner :

1°. Son étendue ;

2°. L'explication qu'elle donne des faits ;

3°. La manière dont elle donne cette explication.

Quant au premier point, la théorie unitaire met chaque combinaison chimique dans certains rapports de comparaison avec tous les autres. C'est là que se trouve en apparence son mérite. Cependant si nous approfondissons l'examen de cette théorie, nous trouverons que ce mérite même est fatal pour elle.

Le point de vue qu'elle prend pour ses comparaisons, est un point de vue essentiellement pernicieux.

Pour le second point, elle n'explique pas les faits du tout, de sorte que la condition la plus importante n'est pas remplie.

La deuxième condition n'étant pas remplie, la troisième ne l'est pas davantage.

Comment se fait-il que la théorie de Gerhardt ne réponde pas, sur ces points essentiels, aux exigences de la philosophie ?

C'est parce qu'elle est basée sur un principe ancien mais vicieux, qui a autrefois retardé la science pendant des siècles.

Elle prend pour point de départ une généralisation dont elle déduit ensuite tous les cas particuliers. Mais ce n'est pas dans un travail chimique qu'il est possible d'entreprendre une discussion purement métaphysique, quoique la théorie de Gerhardt ne puisse être combattue efficacement que par des raisons métaphysiques, puisqu'elle ne peut être mise en avant qu'en renversant un principe général des recherches scientifiques.

La généralisation qui fait le fond du système de Gerhardt n'a pas même le mérite d'être représentée par un type ayant une existence connue. $n\mathrm{O}^{\mathrm{H}}_{\mathrm{H}}$, dont il dérive tous les composés chimiques, étant lui-même indéfini, ne peut être contenu dans aucun corps défini. Cependant on a le droit de demander à un type de fournir en lui-même au moins un exemple de ce qu'il est censé représenter. Or la portion n du type représente l'idée de multiples indéfinis de $\mathrm{O}^{\mathrm{H}}_{\mathrm{H}}$, et non-seulement il n'existe pas de multiples de $\mathrm{O}^{\mathrm{H}}_{\mathrm{H}}$ en série indéfinie, mais on n'a pas même prouvé l'existence d'un seul de ces multiples.

La perfection ou l'imperfection du type qui doit représenter l'idée générale, est toutefois d'une importance relativement inférieure. C'est le principe même de la généralisation qui est essentiellement pernicieux.

Si ce principe était appliqué à la vie ordinaire, on le trouverait tout simplement absurde. Supposez, par exemple, que quelqu'un veuille systématiser la réunion des

systematize the formation of letters into words that formed the contents of a book. Were he to begin by saying that he had discovered a *certain word which would serve as a type, and from which by substitution and double decomposition all the others are to be derived*,—that he by this means not only could form new words, but new books, and books almost *ad infinitum*,—that this word also formed an admirable point of comparison with all the others,—that in all this there were only a few difficulties, but that these might be ingeniously overcome,—he would state certainly an empirical truth. At the same time, however, his method would, judged by the light of common sense, be an absurdity. But a principle which common sense brands with absurdity, is philosophically false and a scientific blunder.

Suppose the book that had formed the basis of this system were a German one, where all the words were found to be composed at least of two letters, still even in this language the viewing and systematizing of words as a series of double decompositions would be no less ridiculous.

The sure and invincible method of arriving at every truth which the mind is capable of discovering is always one and the same. It is that, namely, of throwing away all generalization, of going back to first principles, and of letting the mind be guided by these alone. It is the same in common matters. It is the same in science. To reach the structure of words we must go back, seek out the undecomposable elements, viz., the letters, and study carefully their powers and bearing. Having ascertained these, the composition and structure of every possible word is revealed. It would be well to call to recollection the parallelism of chemical research with that of every other search after truth; for it has been in overlooking this, that in chemistry false and vacillating theories have been advocated and a wrong route so often pursued. In mathematics the starting-point is not generalizations, but axioms, ultimate principles. In metaphysics, Descartes led the way of progress by analysing till he thought he could reach some ultimate elements beyond which it was impossible for him to go, then studying their force and power, and proceeding synthetically. The recognition of this method wrought the regeneration of science and philosophy.

On the other hand, look where Gerhardt's generalization of Williamson's generalization leads him, and legitimately too,—a fact which his logical spirit clearly discerned. He is led not to explain bodies according to their composition and inherent properties, but to think it necessary to restrict chemical science to the arrangement of bodies according to their decomposition, and to deny the possibility of our comprehending their molecular constitution. Can such a view tend to the advancement of science? Would it not be only rational, in accepting this veto, to renounce chemical research altogether?

These reflections naturally lead to the inquiry after another theory more adequate to satisfy the just demands which can be made upon it. There is one which, as it is still supported by many distinguished chemists, cannot be passed over altogether unnoticed. It is that of the theory of certain combinates in organic chemistry which are to be viewed as analogous to, "playing the part of," inorganic elements. These are denominated radicals, and are supposed to be contained in all organic chemical products.

In addition to this, and also in connexion with it, there is a doctrine describing many combinates to be copulated, conjugated, by addition.

lettres en mots formant un livre. S'il commençait par dire qu'il a découvert un certain mot pouvant servir de type, duquel tous les autres peuvent se dériver par substitution et par double décomposition, que par ces moyens on peut former non-seulement des mots nouveaux, mais des livres en quantité presque infinie, que ce mot forme ainsi un admirable point de comparaison pour tous les autres, que dans tout cela il n'y a que quelques difficultés peu nombreuses pouvant être ingénieusement tournées, cet homme établirait certainement une vérité experimentale. Cependant, en même temps, sa méthode, jugée à la lumière du sens commun, serait une absurdité. Or un principe condamné par le sens commun est philosophiquement faux et ne peut être qu'une erreur scientifique.

Supposez que le livre pris pour base du système dont nous venons de parler, soit un livre allemand, où tous les mots sont composés au moins de deux lettres ; même dans cette langue il serait ridicule de considérer les mots comme résultant de séries de doubles décompositions.

La méthode sûre et infaillible d'arriver à toute espèce de vérité est toujours la même. Elle consiste en particulier à mettre de côté toute généralisation, à remonter aux premiers principes, et à prendre ceux-ci pour seuls guides de l'esprit. Ceci est vrai pour les affaires ordinaires, et tout autant pour la science.

Pour étudier la structure des mots, il faut remonter aux éléments indécomposables des mots, aux lettres, et se rendre compte soigneusement de leurs propriétés.

Celles-ci une fois établies, la composition de tout mot possible est expliquée.

Il serait utile de rappeler la nécessité de suivre, en chemie, la même marche que dans tout autre genre de recherche de la vérité ; car c'est en oubliant cette nécessité, qu'on a défendu, en chimie, des théories fausses et vacillantes, et qu'on a tant de fois marché dans une mauvaise voie.

En mathématiques, le point de départ ne se trouve pas dans des généralisations, mais dans des axiomes. En métaphysique, Descartes a montré le chemin du progrès en continuant son analyse jusqu'à ce qu'il crut avoir atteint des éléments derniers, au delà desquels il lui était impossible d'aller, en étudiant ensuite leurs forces et leurs propriétés, et en procédant enfin par synthèse. C'est le triomphe de cette méthode qui a régénéré la science et la philosophie.

D'un autre côté, voyez où Gerhardt est conduit par sa généralisation d'une première généralisation de Williamson : il arrive nécessairement à un fait que son esprit logique lui a clairement montré ; il renonce à expliquer la constitution des corps d'après leur composition et leurs propriétés inhérentes, et croit nécessaire de restreindre la chimie à un arrangement systématique des corps d'après leurs décompositions, niant même la possibilité de comprendre leur constitution moléculaire. Une semblable manière de voir peut-elle tendre à l'avancement de la science ? et ne serait-il pas raisonnable devant un pareil *veto*, de renoncer complétement aux études chimiques ?

Ces réflexions conduisent naturellement à rechercher une théorie répondant mieux aux justes exigences de la raison. Il en est une, appuyée encore par beaucoup de chimistes distingués, que nous ne pouvons pas passer sous silence. C'est celle qui regarde certains composés de la chimie organique comme analogues aux corps simples de la chimie minérale, et jouant le même rôle qu'eux. Ces corps sont appelés *radicaux*, et on en admet l'existence dans tous les composés organiques.

Il se lie à cette théorie une doctrine, qui regarde beaucoup de combinaisons comme copulées ou conjuguées par addition.

It is impossible here to enter upon any extensive criticism of this theory. I can only remark that it is not merely an unprofitable figure of language, but is injurious to science, inasmuch as it tends to arrest scientific inquiry by adopting the notion that these quasi elements contain some unknown and ultimate power which it is impossible to explain. It stifles inquiry at the very point where an explanation is demanded, by putting the seal of elements, of ultimate powers, on bodies which are known to be anything but this.

Science demands the strict adherence to a principle in direct contradiction to this view. That first principle, without which research cannot advance a step, dare not be ignored; namely, that a whole is simply a derivative of its parts. As a consequence of this, it follows that it is absolutely necessary to scientific unity and research to consider these bodies as entirely derivative, and as containing no secret ultimate power whatever, and that the properties which these so-called quasi elements possess are a direct consequence of the properties of the individual elements of which they are made up.

Nor is the doctrine of bodies being "conjugated by addition" a whit in advance of that which I have just been considering. This doctrine adopts the simple expedient of dividing certain combinates, if possible, into two imaginary parts, of which one or both are bodies already known. Then it tells us that these two parts are found united in this body. But how they are united, or what force binds them together, it does not inquire. Is this explication arbitrary? Is it instructive? Is it science?

I may now be permitted to submit a few considerations relative to a more rational theory of chemical combination.

As everything depends upon the method of research employed, it will in the first place be necessary to find one that may be relied upon. If the method is good, and conscientiously carried out, stable and satisfactory results may be expected. If, on the contrary, it is vicious, we can only expect a corresponding issue. A satisfactory method is, however, not difficult to find, nor is it difficult in its application.

The principle which ought to guide all research is in every case the same. It is that of analysing till it is impossible to reach more simple elements, and of studying these elements in all their properties and powers. When all the properties and powers of the individual elements are known, then it will be possible to know the constitution of the combinates which their synthesis produces. It is necessary therefore in chemical research, in order to ascertain the various qualities and functions of the different elements,—

1. To consider the whole of chemistry as one.

2. To take into consideration every known combinate, and to study the character, functions, and properties displayed by each element for itself, in each of these combinates in all their different conditions and aspects It is by a comparison of the different bodies among themselves that we are able to trace the part that is performed by each element separately.

3. To trace the general principles common to all the elements, noting the special properties of each.

This method is essentially different from that where one class of bodies is

Il est impossible d'entrer ici dans une critique détaillée de cette théorie. Je dois me borner à faire remarquer qu'elle n'est pas seulement une manière de parler inutile, mais qu'elle nuit encore à la science en tendant à arrêter l'analyse scientifique par l'idée que ces quasi-éléments renferment quelque force dernière inconnue, qu'il est impossible d'expliquer.

En donnant le caractère d'éléments, de forces dernières à des corps qu'on sait n'être rien moins que cela, elle arrête les recherches au point même dont on demande l'explication.

La science réclame une stricte fidélité à un principe directement opposé à cette manière de voir. Ce principe, sans lequel les recherches scientifiques ne peuvent pas faire un pas, c'est qu'un tout est simplement un dérivé de ses parties.

Comme conséquence, il en résulte qu'il est absolument nécessaire pour l'unité de la science et pour le progrès des recherches de considérer ces corps qu'on a appelé *radicaux*, comme dérivés et comme ne renfermant aucune force dernière cachée, et d'admettre que leurs propriétés sont une conséquence directe des propriétés individuelles des éléments qui les composent.

La doctrine des corps conjugués par addition n'est pas un progrès sur celle que nous venons de considérer. Cette doctrine adopte le simple expédient de diviser, lorsque c'est possible, certains composés en deux portions imaginaires, dont l'une ou bien toutes deux sont des corps déjà connus. Elle déclare ensuite que ces deux corps se trouvent unis dans le composé en question. Mais elle ne s'inquiète pas de savoir comment elles sont unies ou quelle force les lie. Cette explication n'est-elle pas arbitraire ? Nous apprend-elle quelque chose ? Est-ce là de la science ?

Il me sera permis maintenant de faire valoir quelques considérations relatives à une théorie plus rationelle des combinaisons chimiques.

Comme tout dépend de la méthode de recherche employée, il est avant tout nécessaire d'en trouver une dans laquelle nous puissions avoir confiance. Si la méthode est bonne et si elle est appliquée consciencieusement, nous pouvons en attendre des résultats certains et satisfaisants. Si au contraire elle est vicieuse, nous ne pouvons attendre qu'un mauvais résultat. Heureusement, il n'est pas difficile de trouver une bonne méthode, qui ne présente pas de difficultés dans son application.

Le principe qui doit guider toutes les recherches est dans tous les cas le même. C'est celui d'analyser jusqu'à ce qu'il soit impossible d'atteindre des éléments plus simples, et d'étudier ces éléments dans leurs propriétés et leurs forces. Les forces et les propriétés des éléments étant toutes connues, il sera possible alors de connaître la constitution des combinaisons produites par leur synthèse.

Il est donc nécessaire, dans les recherches chimiques, pour s'assurer des propriétés et des fonctions des différents éléments :

1°. De considérer la chimie comme formant un ensemble unique.

2°. D'étudier tous les composés connus et de se rendre compte du caractère, des fonctions et des propriétés de chaque élément, dans chaque composé, sous tous les points de vue et dans toutes les conditions différentes.

C'est par la comparaison des différents corps entre eux que nous pouvons reconnaître le rôle que joue chaque élément séparément.

3°. De rechercher les principes généraux communs à tous les éléments, en prenant note des propriétés spéciales de chacun d'eux.

Cette méthode est essentiellement différente de celle où une classe de corps est

chosen as a point for the restriction of our views of the properties of the others—where only the qualities found in the first are to be measured out to the rest.

I shall now proceed to inquire how its more thorough application tends to the development of a rational chemical theory.

It has been found that there is one leading feature, one inherent property, common to all the elements. It has been denominated chemical affinity. It is discovered under two aspects:—(1) affinity of kind; (2) affinity of degree.

Affinity of kind is the special affinities manifested among the elements, the one for the other, etc., as carbon for oxygen, for chlorine, for hydrogen, etc.

Affinity of degree is the grades, or also limits of combination, which the elements display. For instance, C^2O^2 and C^2O^4 are the degrees of affinity of carbon for oxygen. C^2O^2 may be called the first degree, and C^2O^4 may be termed the second degree, and, as a higher degree than this is not known for carbon, its ultimate affinity or combining limit. Affinity of degree in an element may have only one grade. It may have, however, and generally has more than one. Here then is an inherent property common to all elements, by the removal of which the chemical character of an element will be destroyed, and by virtue of which an element finds its place marked out in a complex body.

It is such a property that is required to form the base of a system. Nor would its suitableness for this purpose be affected by the discovery that the elements are themselves composite bodies, which view the chemist is perhaps not unwarranted to adopt. For, in such a case, the necessity would doubtless still be found to exist of adopting the principle of affinity, or something at least equivalent to it, as the basis of the explanation of chemical combinates. In applying this method, I propose at present to consider the single element carbon. This body is found to have two highly distinguishing characteristics:—

1. It combines with equal numbers of hydrogen, chlorine, oxygen, sulphur, etc.
2. It enters into chemical union with itself.

These two properties, in my opinion, explain all that is characteristic of organic chemistry. This will be rendered apparent as I advance.

This second property is, so far as I am aware, here signalized for the first time. Evidence as to its being a property of carbon may therefore be required.

It will be found in the following:—What is the link which binds together bodies composed of 4, 6, 8, 10, 12, etc., equivalents of carbon, and as many equivalents of hydrogen, oxygen, etc.? In these you may remove perhaps all the hydrogen or oxygen, and substitute so many equivalents of chlorine, etc. It is then the carbon that is united to carbon. Further, that it is not the hydrogen that is the binding element in these combinates is evident; thus—

choisie pour restreindre nos idées sur les propriétés des autres corps, et où celles seulement reconnues dans les premiers sont accordées aux derniers.

Je vais maintenant chercher comment l'application plus complète de cette méthode conduit au développement d'une théorie rationnelle de la chimie.

On a trouvé qu'il existe un trait saillant, une propriété commune à tous les éléments. On a appelé cette propriété *affinité chimique.* Elle se présente de deux manières différentes :

1°. Elle peut s'exercer comme affinité élective ;

2°. Elle peut s'exercer comme affinité de degré.

L'affinité élective est l'affinité que les éléments montrent les uns pour les autres : ainsi le carbone pour l'oxygène, pour le chlor, pour l'hydrogène, etc.

L'affinité de degré est l'affinité qui s'exerce entre deux éléments en proportions multiples ; ce sont des limites de combinaison. Par exemple C^2O^2 et C^2O^4 sont les degrés de l'affinité du carbone pour l'oxygène.* On peut appeler, C^2O^2 premier degré, et C^2O^4 second degré, et comme on ne connaît pas, pour le carbone, de degré plus élevé, affinité dernière ou limite de combinaison. L'affinité de degré, pour un élément, peut n'avoir qu'un degré. Cependant elle peut en avoir et en a généralement plus d'un.

C'est donc là une propriété inhérente aux éléments, qui leur est commune à tous, et dont la suppression entraînerait la destruction du caractère chimique de l'élément ; elle marque à chaque élément sa place dans un corps composé.

Il faut une propriété de ce genre pour former la base d'un système ; elle resterait encore suffisante pour cela, quand bien même on découvrirait, ce que les chimistes n'ont pas le droit de regarder comme impossible, que les éléments eux-mêmes sont des corps composés ; car dans ce cas, sans aucun doute, on se trouverait encore dans la nécessité d'adopter le principe de l'affinité ou de moins quelque chose d'équivalent, comme base de l'explication des combinaisons chimiques.

Pour le moment toutefois, il est impossible de remonter à des éléments plus simples. Il est donc nécessaire provisoirement de partir des affinités et des propriétés découvertes dans les éléments, pour arriver à la théorie de leurs combinaisons.

Comme application de cette méthode, considérons maintenant le seul élément carbone. Ce corps possède deux caractères qui le distinguent particulèrement :

1°. Il entre en combinaison avec des nombres égaux d'équivalents d'hydrogène, de chlor, d'oxygène, de soufre, etc.

2°. Il entre en combination avec lui-même.

Dans mon opinion, ces deux propriétés suffisent pour expliquer tout ce que la chimie organique présente de caractéristique ; c'est que je démontrerai plus loin.

La seconde de ces propriétés est, je crois, signalée ici pour la première fois.

On peut demander de prouver que ce soit là une propriété du carbone. Ce qui suit va le démontrer. Quel est le lien qui tient ensemble les composés de 4, 6, 8, 10, 12, etc., molécules de carbone et d'un pareil nombre d'équivalents d'hydrogène, d'oxygène, etc. ? On peut enlever de ces composés tout l'hydrogène et tout l'oxygène peut-être, et le remplacer par autant d'équivalents de chlor, etc. C'est donc le carbone qui est uni au carbone. De plus, il est évident que ce n'est pas l'hydrogène qui sert de lien dans les combinaisons, car on a

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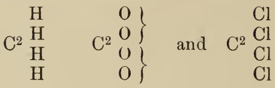
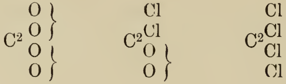
* Misprinted "l'hydrogène" in the original. See the English paper.



$$C^2\begin{matrix}H\\H\\H\\H\end{matrix}\qquad C^2\begin{matrix}\left.\begin{matrix}O\\O\end{matrix}\right\}\\\left.\begin{matrix}O\\O\end{matrix}\right\}\end{matrix}\qquad \text{and}\qquad C^2\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}$$

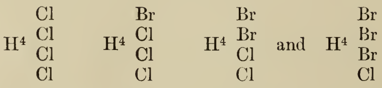
Here the whole four of hydrogen are not bound by a mutual affinity; for each element of hydrogen can be substituted for one of chlorine in regular series, beginning with the first and ending with the last. The atoms of oxygen are, on the contrary, united in pairs (which will be more fully developed hereafter), and only for two atoms of oxygen two of chlorine can be substituted; thus—



$$C^2\begin{matrix}\left.\begin{matrix}O\\O\end{matrix}\right\}\\\left.\begin{matrix}O\\O\end{matrix}\right\}\end{matrix}\qquad C^2\begin{matrix}Cl\\Cl\\\left.\begin{matrix}O\\O\end{matrix}\right\}\end{matrix}\qquad C^2\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}$$

In the same manner, with bodies that contain multiples of C^2 united to hydrogen, etc.

Take the inverse of this. If the four atoms of hydrogen were bound together, we could evidently expect to form such bodies as



$$H^4\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\qquad H^4\begin{matrix}Br\\Cl\\Cl\\Cl\end{matrix}\qquad H^4\begin{matrix}Br\\Br\\Cl\\Cl\end{matrix}\quad \text{and}\quad H^4\begin{matrix}Br\\Br\\Br\\Cl\end{matrix}$$

or for bodies like C^4H^4, C^6H^6, C^8H^8, one would naturally expect to find the carbon substituted for chlorine, and find bodies like $H^4\begin{matrix}Cl^2\\Cl^2\end{matrix}$*, H^6Cl^6, H^8Cl^8, etc.

These bodies are not only unknown, but the whole history of hydrogen might be investigated and not a single instance be found to favour the opinion that it has any affinity for itself when in union with another element.

Now, on the other hand, carbon remains chemically united to carbon, while perhaps 8 equivalents of hydrogen are exchanged for 8 equivalents of chlorine, as in naphthaline. Analogous to this is the conversion of alcohol, $C^4\begin{matrix}O\cdots OH\\H^5\end{matrix}$, and the hydrocarbide C^4H^6 into C^4Cl^6. All the countless instances of substitution of chlorine, etc., tend in the same direction. They prove beyond doubt that carbon enters into chemical union with carbon, and that in the most stable manner. This affinity, one of the strongest that carbon displays, is perhaps only inferior to that which it possesses for oxygen.

Another feature in the affinity of carbon is, that it combines by degrees of two; thus, C^2O^2 and C^2O^4, C^4H^4 and C^4H^6, C^6H^6 and C^6H^8, C^8H^8 and C^8H^{10}, etc.: from these last it is especially evident that two is the combining grade of carbon. It becomes still more apparent when we compare the bodies C^4H^4 and C^4H^5Cl, that is, $\left.\begin{matrix}Cl\\C^4H\\H^4\end{matrix}\right\}$ etc. Many such proofs might be added, while, on the

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* Misprinted "C^2" in the original. See the French paper.

$$C^2\left\{\begin{array}{l}H\\H\\H\\H\end{array}\right\}, \qquad C^2\left\{\begin{array}{l}\left.\begin{array}{l}O\\O\end{array}\right\},\\\left.\begin{array}{l}O\\O\end{array}\right\},\end{array}\right. \qquad C^2\left\{\begin{array}{l}Cl\\Cl\\Cl\\Cl\end{array}\right\}.$$

Ici les 4 molécules d'hydrogène ne sont pas liées ensemble par une affinité mutuelle, car chaque élément d'hydrogène peut être remplacé par un élément de chlore, en commençant par le premier et finissant par le dernier. Les atomes d'oxygène sont, au contraire, unis par paires (c'est ce qui sera plus complétement développé plus bas), et on ne peut remplacer que 2 molécules d'oxygène par 2 de chlore.

Ainsi

$$C^2\left\{\begin{array}{l}\left.\begin{array}{l}O\\O\end{array}\right\},\\\left.\begin{array}{l}O\\O\end{array}\right\},\end{array}\right. \qquad C^2\left\{\begin{array}{l}\left.\begin{array}{l}Cl\\Cl\end{array}\right\},\\\left.\begin{array}{l}O\\O\end{array}\right\},\end{array}\right. \qquad C^2\left\{\begin{array}{l}\left.\begin{array}{l}Cl\\Cl\end{array}\right\},\\\left.\begin{array}{l}Cl\\Cl\end{array}\right\}.\end{array}\right.$$

Il en est de même pour les corps qui renferment des multiples de C^2 unis avec de l'hydrogène, etc.

Prenons l'inverse de ce raisonnement. Si les 4 atomes d'hydrogène étaient unis ensemble, nous aurions le droit d'attendre la formation de corps tels que

$$H^4\left\{\begin{array}{l}Cl\\Cl\\Cl\\Cl\end{array}\right\}, \qquad H^4\left\{\begin{array}{l}Br\\Cl\\Cl\\Cl\end{array}\right\}, \qquad H^4\left\{\begin{array}{l}Br\\Br\\Cl\\Cl\end{array}\right\}, \qquad H^4\left\{\begin{array}{l}Br\\Br\\Br\\Cl\end{array}\right\},$$

ou bien pour des corps tels que C^4H^4, C^6H^6, C^8H^8, on s'attendrait naturellement à voir le carbone remplacé par du chlor et à trouver des corps tels que H^4Cl^4, H^6Cl^6, H^8Cl^8, etc.

Non-seulement ces corps sont inconnus, mais on pourrait encore étudier toute l'histoire de l'hydrogène sans trouver un seul exemple en faveur de l'opinion qu'il aurait quelque affinité pour lui-même, lorsqu'il est combiné avec un autre élément.

On peut remarquer aussi que le carbone reste chimiquement combiné avec lui-même, pendant que peut-être huit atomes d'hydrogène sont remplacés par huit atomes de chlore, comme dans la naphtaline.

La transformation de l'alcool $C^4{}^{O-OH}_{\;H^5}$ et du carbure d'hydrogène C^4H^6 en chlorure de carbone C^4Cl^6, sont des faits analogues.

Ainsi que tous les nombreux exemples de substitution de chlore, les faits précédents prouvent, sans qu'il soit possible de conserver aucun doute, que le carbone s'unit chimiquement avec le carbone, et cela de la manière la plus stable. Cette affinité, l'une des plus énergiques parmi celles que montre le carbone n'est peut-être inférieure qu'à celle qu'il a pour l'oxygène.

Un autre trait saillant de l'affinité du carbone est le suivant : il se combine par degrés pairs. Ainsi on a C^2O^2 et C^2O^4,—C^4H^4 et C^4H^6,—C^6H^6 et C^6H^8,—C^8H^8 et C^8H^{10}, etc. Ces derniers composés, en particulier, prouvent évidemment que le carbone se combine avec des nombres pairs d'atomes.

Cette proprieté devient encore plus évidente lorsque nous comparons les corps C^4H^4 et C^4H^5Cl, ou $C^4\left\{\begin{array}{l}Cl\\H\\H^4\end{array}\right\}$, etc.

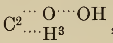
other hand, there are no instances contradictory of this point. Hence the circumstance that it must ever remain impossible to isolate a combinate of the form C^2H^3 or C^4H^5, etc.

Carbon having only two grades of combination of two atoms each, a fact which is easily traced throughout all organic chemistry, this inherent property of the element may legitimately furnish two grand types for all its combinates.

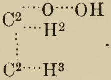
The first type will be nC^2M^4.

The second type will be $nC^2M^4 — mM^2$.*

As examples belonging to the first type, may be mentioned the alcohols of the æthylic form, their æthers, the fatty acids, etc.

Thus methylic alcohol has the formula  $C^2\begin{array}{l}\cdots O\cdots OH\\ \cdots H^3\end{array}$,

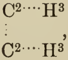
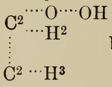
and æthylic alcohol,

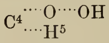


$$\begin{array}{l} C^2\begin{array}{l}\cdots O\cdots OH\\ \cdots H^2\end{array}\\ \vdots\\ C^2\cdots H^3\end{array}.$$

In these instances it will be observed, that for each double atom of carbon the combining power is (4) four, which is the ultimate limit of combination for carbon in all bodies yet produced.

In the latter instance it is apparent, inasmuch as if the combining limit of two C^2s be each reduced by 3 in hydrogen or oxygen, there still remains a combining power of *one* to each of the two C^2 which each expends in uniting with the other;

therefore  $\begin{array}{l} C^2\cdots H^3\\ \vdots\\ C^2\cdots H^3\end{array}$, or, what is the same thing,  $\begin{array}{l} C^2\begin{array}{l}\cdots O\cdots OH\\ \cdots H^2\end{array}\\ \vdots\\ C^2\cdots H^3\end{array}$ belongs to the type nC^2M^4.

Again, the inherent properties of the elements may be viewed as dividing bodies into primary, secondary, tertiary, and so on, combinates. These may be termed so many orders of complicity. Thus C^4H^6 is a primary combinate, or it belongs to the first order of complicity; but  $C^4\begin{array}{l}\cdots O\cdots OH\\ \cdots H^5\end{array}$ is a secondary combinate, or belongs to the second order of complicity. C^2O^2 and C^2O^4 are primary, while C^2O^4, 2OH and C^2O^4, 2OKa are secondary.

A primary combinate is then nC^2 united to nM^4 or to $nM^4 — mM^2$ in such a

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* Misprinted "mM" in the original.

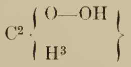
On pourrait ajouter bien d'autres preuves en sa faveur, tandis qu'il n'y a point de faits en contradiction avec elle. Il résulte de là qu'il doit être impossible d'isoler un composé de la forme C^2H^3 ou C^4H^5, etc.

Le carbone ne se combinant qu'en deux degrés différents et chaque fois par deux atomes (fait que l'on peut vérifier aisément dans toute la chimie organique), cette propriété fondamentale de l'élément peut légitimement fournir deux grands types pour toutes les combinaisons dans lequelles il entre.

Le premier type sera nC^2M^4, et le second $nC^2M^4—mM^2$, où m est un nombre moindre que n.

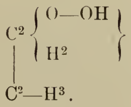
Les alcools de la forme éthylique, leurs éthers, les acides gras, etc., rentrent dans le premier type.

Ainsi l'esprit-de-bois a pour formule



$$C^2\left\{\begin{matrix} O-OH \\ H^3 \end{matrix}\right\}$$

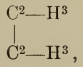
et l'alcool



$$\begin{array}{l} C^2\left\{\begin{matrix} O-OH \\ H^2 \end{matrix}\right\} \\ | \\ C^2-H^3. \end{array}$$

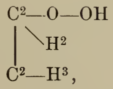
On remarquera que, dans ces exemples, la puissance de combinaison de chaque double atome de carbone est de 4 ; c'est là la dernière limite de combinaison du carbone dans tout les corps obtenus jusqu'à ce jour.

Le dernier exemple montre dans le carbone un même pouvoir de combinaison ; car, en déduisant du pouvoir de combinaison de chacun des doubles atomes de carbone trois forces employées par l'hydrogène et l'oxygène qui leur sont combinés, il reste encore libre une force qui s'exerce dans l'union des doubles atomes l'un avec l'autre ; il en résulte que



$$\begin{array}{l} C^2-H^3 \\ | \\ C^2-H^3, \end{array}$$

ou, ce qui revient au même,



$$\begin{array}{l} C^2-O-OH \\ |\diagdown H^2 \\ C^2-H^3, \end{array}$$

appartient au type nC^2M^4.

On peut considérer les propriétés inhérentes des éléments comme divisant les corps en primaires, secondaires, tertiaires, etc. ; c'est ce qu'on peut appeler les divers degrés de complication. Ainsi C^4H^6 est un composé primaire, c'est-à-dire qu'il appartient au premier degré de complication. Mais $C^4\genfrac{}{}{0pt}{}{O-OH}{H^5}$ est un composé secondaire ou appartient au second degré de complication. C^2O^2 et C^2O^4 sont primaires, tandis que $C^2O^4—O^2H^2$ et $C^2O^4—O^2K^2$ sont secondaires.

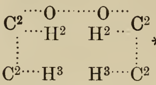
Une combinaison primaire est donc composée de nC^2 uni à nM^4 ou à $nM^4—mM^2$,

manner that the combining energy of the complement (nM^4, etc.) either *potentially or actually* does not extend beyond nC^2.

A secondary combinate is one in which the combining energy of the complement is not all expended upon nC^2, but is extended further to one or more elements.

On the same principle there are tertiary combinates, etc.

These orders of complicity ought in reality to be subdivided. This, however, I do not think it necessary for the present to enter upon. It will now be understood why an alcohol belongs to the type nC^2M^4, and on the same principle why a free æther belongs to the same type, thus



$$\begin{array}{lcr} C^2 \cdots O \cdots\cdots & & O \cdots C^2 \\ \vdots \quad \cdots H^2 & & H^2 \cdots \quad \vdots \\ C^2 \cdots H^3 & & H^3 \cdots C^2 \end{array}$$

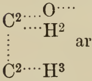
*, while they are at the same time secondary combinates.

A secondary combinate, that is to say, a body belonging to the second order of complicity, is, as will be understood from the principle which forms the ground of the rational theory, a direct consequence of an inherent property of one or more of the elements which form the complement to the carbon.

In the instance before us, it is a certain property of the oxygen which is the cause of the secondary combinate. This property is the affinity which one atom of oxygen in combination always exerts towards another atom of oxygen likewise in combination.

This affinity is modified by the electric position of the element to which the respective atoms of oxygen are bound. From this property results the fact, that in organic combinates the atoms of oxygen are always found double.

For instance, the combining limit of oxygen being two, when two molecules of

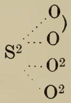


$$\begin{array}{l} C^2 \cdots O \cdots \\ \vdots \quad \cdots H^2 \\ C^2 \cdots H^3 \end{array}$$

are set at liberty, the free affinities of the oxygen instantly produce the union of these molecules. The cause of the union of two molecules of C^2H^3 has been already remarked. In the two cases, the causes of the union of the respective molecules are in so far different, that the one is the result of a property of the carbon, while the other is the result of a property of the oxygen.

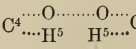
The view here adopted of the nature of oxygen is, I am convinced, alone in conformity with the reactions where the properties of this body develope themselves.

The vapour of anhydrous sulphuric acid, for instance, is conducted into anhydrous æther. The following will then be the reaction :—



$$S^2 \begin{array}{l} \cdots O \\ \cdots O \\ \cdots O^2 \\ \cdots O^2 \end{array}$$

entering into communication with



$$C^4 \begin{array}{l} \cdots O \cdots\cdots O \cdots \\ \cdots H^5 \quad H^5 \cdots \end{array} C^4,$$

the two atoms of the oxygen of the sulphuric acid

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* The vertical dotted line between these two "C^2's" is omitted in the original.

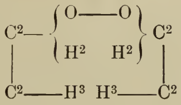
de telle sorte que le pouvoir de combinaison du complément (nM^4), soit virtuellement, soit actuellement, ne dépasse pas celui de nC^2.

Les combinaisons secondaires sont celles où le pouvoir de combinaison du complément, au lieu de se porter entièrement sur nC^2, s'étend encore sur un ou plusieurs autres éléments

Il existe de même des combinaisons tertiares, etc.

Ces degrés de complication devraient à la rigueur être subdivisés. Toutefois je ne crois pas nécessaire, pour le moment, d'entrer dans ces détails.

On comprendra maintenant comment un alcool appartient au type nC^2M^4, ainsi qu'un éther libre ; par exemple,



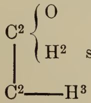
$$\begin{array}{l} C^2 - \left\{\begin{array}{c} O \text{------} O \\ H^2 \quad H^2 \end{array}\right\} C^2 \\ | \qquad\qquad\qquad\qquad | \\ C^2\text{------}H^3 \quad H^3\text{------}C^2 \end{array}$$

et que tous deux sont des composés secondaires.

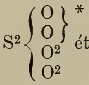
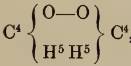
Les combinaisons secondaires, c'est-à-dire les corps appartenant au second degré de complication, prennent naissance (on le comprendra en partant du principe qui forme la base de la théorie rationelle), en vertu d'une propriété appartenant à un ou plusieurs des éléments combinés avec le carbone.

Dans les exemples précédents, c'est une certaine propriété de l'oxygène qui est cause de la complication du corps. Cette propriété consiste dans l'affinité qu'une molécule d'oxygène en combinaison excerce toujours sur une seconde molécule d'oxygène elle-même combinée. Cette affinité est modifiée par l'état (électrique ?) des éléments auxquels les deux atomes sont liés.

Il résulte de là que, dans les composés organiques, les atomes d'oxygène vont toujours par deux.

Par exemple, le pouvoir de combinaison de l'oxygène étant 2, quand 2 molécules de  $\begin{array}{l} C^2 \left\{\begin{array}{l} O \\ H^2 \end{array}\right. \\ | \\ C^2\text{------}H^3 \end{array}$ sont mises en liberté, l'affinité non satisfaite de l'oxygène produit immédiatement l'union de ces molécules. On a déjà vu la cause de l'union de deux molécules de C^2H^3. Dans ce dernier cas, l'union des molécules est due à une propriété du carbone, et dans le premier à une propriété de l'oxygène.

Les vues emises ici sur la nature et les fonctions de l'oxygène sont, j'en suis convaincu, seules conformes aux réactions dans lesquelles les propriétés de ce corps sont en jeu.

Par exemple, on fait arriver la vapeur d'acide sulfurique anhydre dans de l'ether anhydre. Voici quelle sera la réaction :  $S^2\left\{\begin{array}{l}\left.\begin{array}{l}O\\O\end{array}\right\}^{*}\\O^2\\O^2\end{array}\right.$ étant mis en présence de  $C^4\left\{\begin{array}{c}O\text{---}O\\H^5\,H^5\end{array}\right\}C^4$, les deux atomes d'oxygène de l'acide sulfurique et les deux atomes

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* The two upper " O's " have been omitted in the original. See the English paper.

and the two atoms of the oxygen of the æther (now in presence of each other) being in different (perhaps different electric) conditions, mutually loosen their former affinities and reunite themselves to the (electrically ?) different atoms of oxygen of these respective combinates.

The same principle may naturally be expected to display itself with regard to acids and bases. The oxygen of an acid unites itself to the (electrically ?) different oxygen of water. The oxygen of a base on the same principle has an affinity for the electrically different oxygen of water.

It will be observed—

1. That the oxygen of the water of an acid can only be expelled by that of a base and *vice versâ.*

2. It is to be remarked that *it is not* the metal of a base which exchanges places with the hydrogen of the hydrate of an acid; for if that were the case, the affinity of the oxygen of the metal, and also of the acid, *would be greater for the oxygen of the water* than the affinity of the hydrogen for that same oxygen. But this is not so. The very opposite is the truth. If one atom of hydrogen be withdrawn from the hydrate of an acid or from *the hydrate of an oxide, it is universally accompanied by an atom of oxygen.* It is evident, then, that the affinity between *the positive and negative atoms of oxygen is less than that which attaches these atoms to the element with which they form a primary combinate.*

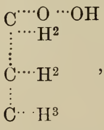
A consequence of this truth is, that it is impossible to double the equivalent of oxygen, if the chemical equivalents are to be understood as not being in direct contradiction to any chemical truth or essential feature in the properties of an element. Carbon differs entirely in this respect from oxygen.

There is no reaction found where it is known that C^2 is divided into two parts. It is only consequent therefore to write, with Gerhardt, C^2 simply as C, it being then understood that the equivalent of carbon is (12) twelve.

This value of the atom will be adopted in the following part of this paper.

Sulphur, selenium, etc., being bodies displaying properties similar, not to carbon, but to oxygen, it will be necessary to retain the equivalent value that has generally been assigned to them.

I have now shown how ordinary alcohol, $C^2H^6O^2$ common æther, and the hydrocarbide, C^2H^6, belong to the type nCM^4. The phenomena which necessitate this view of the constitution of these bodies have a like consequence in regard to the other alcohols, glycols, acids, and æthers of this series.

Propyle alcohol is  $\begin{array}{l} C\cdots O\cdots OH \\ \vdots\cdots H^2 \\ C\cdots H^2 \\ \vdots \\ C\cdots H^3 \end{array}$, where it will be seen that the atom of carbon situated between the two others, on account of being chemically united to these, is reduced to the combining power of two for hydrogen, oxygen, etc. One combining power is given up to the carbon upon the one side, and a second to the carbon upon the other.

It will be observed also that the primary combinates ought in rigour to be themselves enumerated in an inverse order. The type nCM^4 becomes then in reality the

d'oxygène de l'éther se trouvant dans un état (peut-être électrique) différent, les affinités mutuelles des atomes d'oxygène d'un même corps s'affaiblissent, et ils s'unissent aux atomes (électriquement ?) differents d'oxygène de l'autre composé.

La même chose se passe naturellement entre les acides et les bases. L'oxygène d'un acide s'unit avec l'oxygène (électriquement ?) différent de l'eau. L'oxygéne de la base, en vertu du même principe, s'unit avec l'oxygène (électriquement ?) différent de l'eau.

On remarquera : 1° que l'oxygène de l'eau contenue dans un acide ne pourra être chassé que par celui d'une base ;

2°. Que ce n'est pas le métal de la base qui prend la place de l'hydrogène de l'acide hydraté ; car si cela avait lieu, l'affinité de l'oxygène combiné au métal, ainsi que celle de l'oxygène de l'acide, serait plus grande pour l'oxygène de l'eau que l'affinité de l'hydrogène pour ce même oxygène. Mais il n'en est pas ainsi ; bien au contraire, si un atome d'hydrogène est enlevé à l'acide hydraté ou à une base hydratée, il est universellement accompagné d'un atome d'oxygène. Il est donc évident que l'affinité entre les atomes d'oxygène positif et négatif est moindre que celle qu'ils ont pour l'élément qui forme avec eux un composé primaire.

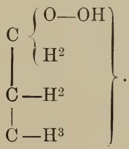
Il résulte de tout ceci, qu'il est impossible de doubler l'équivalent de l'oxygène, si l'on veut que les équivalents chimiques ne se trouve en contradiction avec aucune verité chimique, avec aucun trait essentiel de la physionomie propre d'un élément.

Le carbone diffère complétement sous ce rapport de l'oxygène. On ne connaît pas de réaction où C^2 soit devisé en deux parties. Il faut donc, pour être conséquent, écrire avec Gerhardt C^2 simplement C, en portant à 12 l'équivalent du carbone. C'est cette valeur du poids atomique que nous admettrons dans le reste de ce travail.

Le soufre, le sélénium, etc., étant des corps qui offrent des propriétés semblables à celles de l'oxygène et non à celles du carbone, il sera nécessaire de conserver les équivalents généralement admis.

J'ai montré maintenant comment l'alcool $C^2H^6O^2$, l'éther et le carbure d'hydrogène C^2H^6, appartiennent au type nCM^4. Les phénomènes qui conduisent à cette manière de voir sur la constitution de ces corps ont une conséquence semblable pour les autres alcools, les glycols, les acides, les éthers de cette serie.

L'alcool propylique * est



$$\left.\begin{array}{l} \mathrm{C}\left\{\begin{array}{l}\mathrm{O{-}OH}\\ \mathrm{H}^2\end{array}\right. \\ | \\ \mathrm{C{-}H}^2 \\ | \\ \mathrm{C{-}H}^3 \end{array}\right\}.$$

On remarquera que l'atome de carbone situé entre deux autres, étant chimiquement combiné avec chacun d'eux, son pouvoir de combinaison est réduit à 2 pour l'hydrogène, l'oxygène, etc. Une des forces de combinaison s'exerce sur un élément de carbone d'un côté, et une seconde sur un élément de carbone de l'autre.

Les composés primaires devraient être à la rigueur eux-mêmes énumérés dans un ordre progressif de complication.

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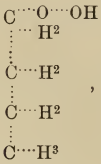
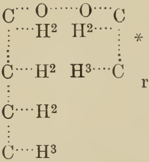
* Misprinted " Le propylglycol " in the original.

type CM^4. This enumeration, however, does not appear to possess any great practical utility, and it is perhaps preferable simply to denote it in an indefinite manner by adding "n" to the true type CM^4.

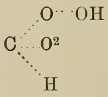
In like manner the butyle alcohol is to be viewed as 

$$\begin{array}{l} C \cdots O \cdots OH \\ \vdots \cdots H^2 \\ C \cdots H^2 \\ \vdots \\ C \cdots H^2 \\ \vdots \\ C \cdots H^3 \end{array}$$

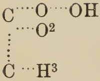
, and so on throughout all the series of these alcohols. The constitution of the æthers will be evident: 

$$\begin{array}{ll} C \cdots O \cdots\cdots O \cdots C & \\ \vdots \cdots H^2 \quad H^2 \cdots \vdots & * \\ C \cdots H^2 \quad H^3 \cdots C & \\ \vdots & \\ C \cdots H^2 & \\ \vdots & \\ C \cdots H^3 & \end{array}$$

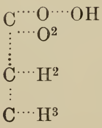
represents the mixed butylic-ethylic æther.

Formic acid is represented by the form 

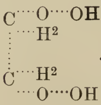
$$\begin{array}{l} \quad O \cdots OH \\ C \cdots O^2 \\ \quad H \end{array}$$

; acetic acid in like manner, 

$$\begin{array}{l} C \cdots O \cdots OH \\ \vdots \cdots O^2 \\ C \cdots H^3 \end{array}$$

. Propionic acid is 

$$\begin{array}{l} C \cdots O \cdots OH \\ \vdots \cdots O^2 \\ C \cdots H^2 \\ \vdots \\ C \cdots H^3 \end{array}$$

. The constitution of glycol may be represented as follows:— 

$$\begin{array}{l} C \cdots O \cdots OH \\ \vdots \cdots H^2 \\ \vdots \\ C \cdots H^2 \\ \quad \cdots O \cdots OH \end{array}$$

.

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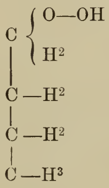
* The vertical dotted lines between the two "C's" is omitted in the original.

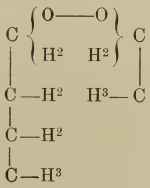
Le type nCM^4 devient alors en réalité le type CM^4. Mais cette énumération ne paraît pas avoir une grande utilité pratique, et il est peut-être préférable de désigner le type d'une manière indéterminée en ajoutant n au vrai type CM^4.

L'alcool butylique est de même représenté par

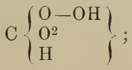


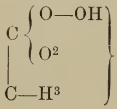
et ainsi de suite en parcourant toute la série de ces alcools.

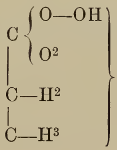
La constitution des éthers n'est pas moins évidente.



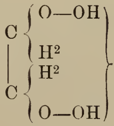
représentera l'éther mixte butyléthylique

L'acide formique sera . .  ;

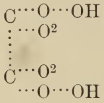
L'acide acétique . . .  .

L'acide propionique . .  .

On peut écrire le glycol ainsi

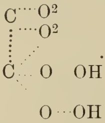
 ,

In like manner as to the acids of these glycols; oxalic acid, for instance, may be represented as



$$\begin{array}{l} C\cdots O\cdots OH \\ \vdots\cdots O^2 \\ \vdots \\ C\cdots O^2 \\ \quad\cdots O\cdots OH \end{array}.$$

Respecting these acids, it may perhaps be allowable to suggest the possibility of the molecule having two poles, and that especially the atom of oxygen situated at one or perhaps both, and near to two atoms of oxygen bound together, and forming no secondary combinate, may be in a state presenting great affinity for basic oxygen. Analogy with electric poles may perhaps demand the opinion that all the negative oxygen be situated upon one side of the molecule. It will in that case be preferable to represent the oxalic acid as



$$\begin{array}{lll} C\cdots O^2 & & \\ \vdots\cdots O^2 & & \\ \vdots & & \\ C\cdots & O & OH \\ & O\cdots & OH \end{array}.$$

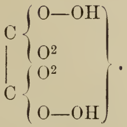
Be that as it may, however, the rational method of investigation proves it to be a law, that in acids of the type nCM^4 the presence of two atoms of oxygen bound together so as to form only a primary part of the same molecule, and situated close to the negative oxygen, is necessary to the calling forth or production of this negative state.

This is a particular instance, but it moreover *shows generally how the electro-positive or the electro-negative value of the elements mutually modify and condition the electropositive or electronegative value* of each other when in combination.

This law is different from the electric hypothesis which chemists have formerly defended, but which never could be traced throughout a thoroughgoing application of their views to organic chemistry.

The law here distinctly enounced coincides exactly with, and is rendered apparent by the application of the theory of chemical combination which I support.

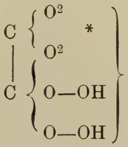
et l'acide oxalique



$$\left.\begin{array}{l} C\left\{\begin{array}{l}O-OH\\ O^2\end{array}\right.\\ | \\ C\left\{\begin{array}{l}O^2\\ O-OH\end{array}\right.\end{array}\right\}.$$

Relativement aux acides, il sera peut-être permis d'émettre la supposition que les molécules possèdent deux pôles, et que la molécule d'oxygène située auprès de l'un des pôles (ou peut-être des deux) et dans le voisinage des deux molécules d'oxygène liées ensemble et ne donnant pas lieu à la formation d'un composé secondaire, que cet oxygène, dis-je, se trouve dans un état tel, qu'il possède une grande affinité pour l'oxygène basique.

L'analogie avec les pôles électriques exige peut-être que tout l'oxygène soit placé d'un côté de la molécule. Il vaudrait mieux, dans ce cas, représenter l'acide oxalique par



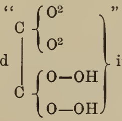
$$\left.\begin{array}{l} C\left\{\begin{array}{l}O^2\\ O^2\end{array}\right. \quad * \\ | \\ C\left\{\begin{array}{l}O-OH\\ O-OH\end{array}\right.\end{array}\right\}$$

Quoi qu'il en soit, la méthode rationelle d'analyse prouve que c'est une loi que, dans les acides du type nCM^4 la présence de deux atomes d'oxygène liés ensemble de manière à former une partie primaire de la même molécule, et situés dans le voisinage de l'oxygène négatif, est nécessaire pour produire dans cet oxygène l'état négatif où il se trouve.

Ceci n'est qu'un cas particulier d'un fait plus général, car il résulte de ce qu'en général l'état électropositif ou électronégatif des éléments modifie ou entraîne l'état électropositif ou électronégatif des éléments combinés avec eux, et réciproquement.

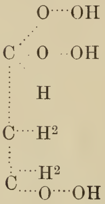
Cette loi diffère de l'hypothèse électrique que les chimistes ont défendue autrefois, mais qui n'a jamais pu recevoir une application complète à leur vues sur la chimie organique.

Celle au contraire que j'énonce ici s'accorde parfaitement avec la théorie que je défends, et s'en déduit d'une manière simple.

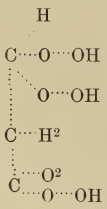


* Misprinted $“\left.\begin{array}{l} C\left\{\begin{array}{l}O^2\\ O^2\end{array}\right. \\ | \\ C\left\{\begin{array}{l}O-OH\\ O-OH\end{array}\right.\end{array}\right\}”$ in the original. See p. 260 and also p. 239.

But to return. Glycerine is



, and glyceric acid



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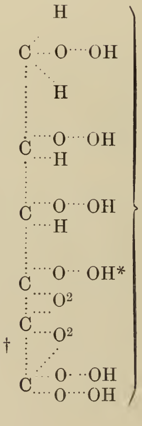
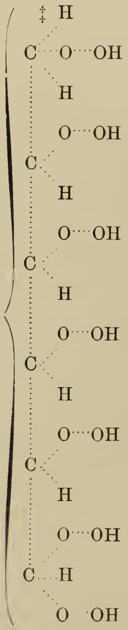
Glucose has been perhaps too little investigated to afford data sufficient to determine definitely its formula. Taking, however, mucic and saccharic acids as starting-points, these bodies may be meanwhile represented as:—



the acids.

Glucose.



It will thus be seen that these combinates all belong to type nCM^4.

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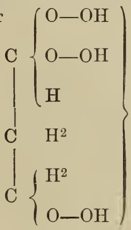
* This "OH" is omitted in the original.

† The oblique dotted line here is omitted in the original.

‡ The vertical dotted line between the "C's" is omitted in the original.

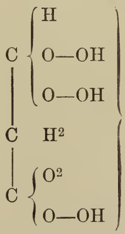
Mais revenons aux formules des combinaisons les plus importantes.

La glycérine est représentée par



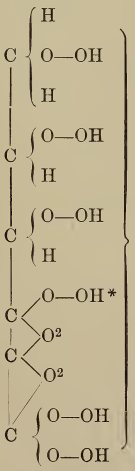
$$\left.\begin{array}{l} C\left\{\begin{array}{l}O—OH\\ O—OH\\ H\end{array}\right.\\ |\\ C\quad H^2\\ |\\ C\left\{\begin{array}{l}H^2\\ O—OH\end{array}\right.\end{array}\right\}$$

et l'acide glycérique par

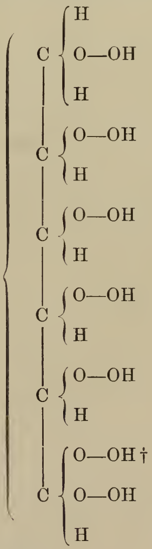


$$\left.\begin{array}{l} C\left\{\begin{array}{l}H\\ O—OH\\ O—OH\end{array}\right.\\ |\\ C\quad H^2\\ |\\ C\left\{\begin{array}{l}O^2\\ O—OH\end{array}\right.\end{array}\right\}$$

La glycose est peut-être trop mal étudiée pour qu'on puisse déterminer définitivement sa formule. Mais en prenant l'acide mucique et l'acide saccharique comme points de départ, ces trois corps peuvent être provisoirement représentés par



Les acides. La glycose.



$$\left\{\begin{array}{l} C\left\{\begin{array}{l}H\\ O—OH\\ H\end{array}\right.\\ |\\ C\left\{\begin{array}{l}O—OH\\ H\end{array}\right.\\ |\\ C\left\{\begin{array}{l}O—OH\\ H\end{array}\right.\\ |\\ C\left\{\begin{array}{l}O—OH\\ H\end{array}\right.\\ |\\ C\left\{\begin{array}{l}O—OH\\ H\end{array}\right.\\ |\\ C\left\{\begin{array}{l}O—OH\,\dagger\\ O—OH\\ H\end{array}\right.\end{array}\right.$$

Il en résulte que ces composés appartiennent au type $n\mathrm{CM}^4$.

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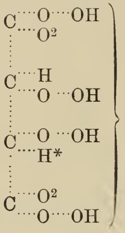
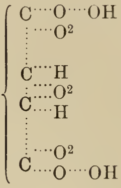
* This "OH" is omitted in the original.

† Misprinted "H" for "O—OH" in the original.

Many others might be added. For instance, tartaric acid :—



And the bibasic acid produced from it by the action of heat will be perhaps



tartrelic acid.

It is my intention to consider, in a future communication, the second type, and to apply my views to the cyanogen combinates, etc.

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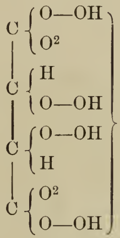
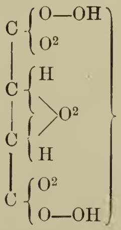
* A horizontal dotted line is erroneously printed here in the original.

On pourrait ajouter beaucoup d'autres corps, par exemple l'acide tartrique :



$$\left.\begin{array}{l} C\left\{\begin{array}{l}O-OH\\O^2\end{array}\right.\\ | \\ C\left\{\begin{array}{l}H\\O-OH\end{array}\right.\\ | \\ C\left\{\begin{array}{l}O-OH\\H\end{array}\right.\\ | \\ C\left\{\begin{array}{l}O^2\\O-OH\end{array}\right.\end{array}\right\}$$

et l'acide bibasique dérivé de l'acide tartrique par l'action de la chaleur sera peut-être



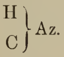
Dans un autre Mémoire je me propose de m'occuper du second type.

En attendant, j'ajouterai seulement la manière dont je considère la constitution des principaux composés cyaniques.

Des raisons entièrement semblables à celles qui me font admettre 4 pour limite du pouvoir de combinaison du carbone, me conduisent à assigner 5 comme limite de combinaison à l'azote. Le premier degré de combinaison de cet élément se rencontre dans l'ammoniaque et équivaut à 3. Le second, qui est égal à 5, se trouve, entre autres composés chimiques, dans le chlorure et dans l'oxyde d'ammonium ainsi que dans l'acide azotique.

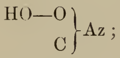
Il résulte de là que le carbone et l'azote combinés, de manière à atteindre tous deux les limites de leur pouvoir de combinaison, formeront un corps dont l'affinité libre s'exercera en fixant un équivalent d'hydrogène ou d'un autre élément.

Ainsi la formule de l'acide cyanhydrique sera



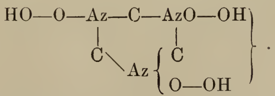
$$\left.\begin{array}{r}H\\C\end{array}\right\}Az.$$

L'acide cyanique sera



$$\left.\begin{array}{r}HO-O\\C\end{array}\right\}Az\ ;$$

l'acide cyanurique



Dans cette dernière formule, les atomes de carbone et d'azote sont liés par 2 unités d'affinité et non par 4, comme dans les deux premiers exemples.

APPENDIX IV *a*.

Recherches sur l'acide salicylique; par M. Couper.*

Les recherches que j'ai honneur de soummettre à l'Académie ont pour objet l'action du perchlorure de phosphore sur le salicylate de méthyle. Je les ai entreprises dans le but de jeter quelque lumière sur une question controversée: la constitution et la basicité de l'acide salicylique.

Une violente réaction se manifeste au contact de l'huile de gaulthéria et du perchlorure de phosphore. Il est nécessaire, pour la maîtriser, d'ajouter par petites portions l'huile essentielle au perchlorure dans le rapport de 1 équivalent du premier corps à 2 équivalents du second. De l'acide chlorhydrique et du chlorure de méthyle se dégagent pendant tout le cours de l'opération.

Le produit obtenu est soumis à la distillation fractionnée. Une trace seulement de chloroxyde passe d'abord, un excès assez considérable de perchlorure de phosphore distille ensuite, et lorsque la température a atteint 160 degrés, le résidu constitue un liquide noir. Si l'on continue la distillation, la température s'élève rapidement à 285 degrés. La plus grande portion du produit passe entre 285 et 295 degrés, sous la forme d'un liquide incolore ou légèrement coloré en jaune. On le recueille séparément. Il reste une masse noire qui se solidifie par le refroidissement.

Le liquide recueilli vers 290 degrés a donné à l'analyse les résultats suivants:

	Expériences.			Théorie.
Carbone . . .	30,86	29,4	29,9	30,65
Hydrogène . . .	1,58†	1,59	1,51	1,46
Chlore . . .	41,01	41,05	...	38,86
Phosphore . . .	12,2	...	...	11,5

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[*] *Comptes rendus*, xlvi., 1107–1110, séance du lundi, 7 juin 1858.

[†] Misprinted in original "1,38" for "1,58". Compare the English text.

APPENDIX IV *b*.

RESEARCHES ON SALICYLIC ACID. BY ARCHIBALD S. COUPER.*

Conflicting opinions being entertained among chemists respecting the constitution and basicity of salicylic acid, in order, if possible, to throw some additional light upon this question, I have been induced to undertake the investigation of the action of two equivalents of pentachloride of phosphorus upon the salicylate of methyl.

When these two bodies are brought into contact, the reaction which ensues is exceedingly violent, and it is necessary to add very gradually the one equivalent of oil of gaultheria to the two equivalents of perchloride of phosphorus. Vapour of hydrochloric acid, mingled with that of the chloride of methyl, is disengaged during the whole course of the operation.

The residue of this reaction is submitted to distillation. A trace of oxychloride passes over, and is followed by something approaching to an equivalent of the perchloride of phosphorus.

The temperature having now risen to about 160°, the residue has darkened in colour. Submitted to a further distillation, a colourless or slightly yellow liquid passes over, while the temperature rises rapidly to about 285° and 295° Cent. The portion passing between these temperatures is collected apart. It constitutes the larger part of the product of distillation. There remains a pitchy residue, which solidifies on cooling. The liquid collected, as described, on being submitted to analysis, furnished the following results :—

1. 0·41 grms. of substance gave 0·464 grms. of carbonic acid, and 0·0585 grms. of water.

2. 0·49 grms. of substance gave 0·528 grms. of carbonic acid, and 0·0705 grms. of water.

3. 0·515 grms. of substance gave 0·565 grms. carbonic acid, and 0·071 grms. of water.

1. 0·438 grms. of substance gave 0·7595 grms. of chloride of silver.

2. 0·34 grms. of substance gave 0·563 grms. of chloride of silver.

1. 0·651 grms. of substance gave 0·283 grms. of the pyrophosphate of magnesia.

These analyses lead to the crude formula,—

$$C^7H^4Cl^3PO^6.$$

	Found.			Calculated.
	I.	II.	III.	
Carbon	30·86	29·4	29·9	30·65
Hydrogen . . .	1·58	1·59	1·51	1·46
Chlorine . . .	41·01	41·05	....	38·86
Phosphorus . . .	12·2	....	....	11·5

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* *The Edinburgh New Philosophical Journal.* New series, vol. viii., July to October 1858, 213–217.

La composition de ce corps est représentée par la formule

$$C^{14}H^{4}Cl^{3}PhO^{6}.$$

Il se forme, en vertu de la réaction suivante :

$$\underbrace{C^{16}H^{8}O^{6}}_{\text{Essence de gaulthéria.}} + PhCl^{5} = HCl + \underbrace{C^{2}H^{3}Cl}_{\substack{\text{Chlorure}\\ \text{de méthyle.}}} + \underbrace{C^{14}H^{4}Cl^{3}PhO^{6}}_{\substack{\text{Trichlorophosphate}\\ \text{de salicyle.}}}$$

Je me suis assuré que le trichlorophosphate de salicyle prend aussi naissance par l'action du perchlorure de phosphore sur l'acide salicylique

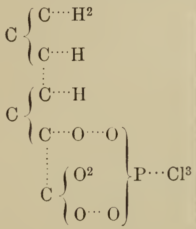
$$\underbrace{C^{14}H^{6}O^{6}}_{\text{Acide salicylique.}} + PhCl^{5} = 2HCl + \underbrace{C^{14}H^{4}Cl^{3}PhO^{6}}_{\text{Trichlorophosphate de salicyle.}}.$$

Entre ces deux corps solides, la réaction est moins violente qu'avec l'essence. Il se dégage de l'acide chlorhydrique, et lorsque l'action est terminée, le résidu est le même que celui qu'on obtient avec l'huile de gaulthéria. Les deux produits distillent exactement de la même manière et à la même température, et les liquides obtenus possèdent la même composition et les mêmes propriétés.

Le trichlorophosphate de salicyle obtenu par l'un ou l'autre de ces procédés se décompose bientôt au contact de l'eau froide et immédiatement lorsqu'on le chauffe avec ce liquide. Les produits de cette réaction sont l'acide chlorhydrique, l'acide phosphorique et l'acide salicylique.

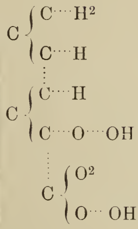
$$\underbrace{C^{14}H^{4}Cl^{3}PhO^{6}}_{\substack{\text{Trichlorophosphate}\\ \text{de salicyle.}}} + 8HO = \underbrace{PhH^{3}O^{8}}_{\text{Ac. phosphorique.}} + 3HCl + \underbrace{C^{14}H^{6}O^{6}}_{\text{Ac. salicylique.}},$$

According to the rational theory which I seek to develop in another paper,* the constitution of this body may be represented as :—



$$\begin{array}{l} C\left\{\begin{array}{l}C\cdots H^2\\ C\cdots H\end{array}\right.\\ \quad\vdots \\ C\left\{\begin{array}{l}C\cdots H\\ C\cdots O\cdots O\end{array}\right.\left.\begin{array}{l}\\ \\ \\ \end{array}\right\} P\cdots Cl^3 \\ \quad\vdots \\ C\left\{\begin{array}{l}O^2\\ O\cdots O\end{array}\right.\end{array}$$

It is a tertiary derivative; the secondary derivative, salicylic acid, being



$$\begin{array}{l} C\left\{\begin{array}{l}C\cdots H^2\\ C\cdots H\end{array}\right.\\ \quad\vdots\\ C\left\{\begin{array}{l}C\cdots H\\ C\cdots O\cdots OH\end{array}\right.\\ \quad\vdots\\ C\left\{\begin{array}{l}O^2\\ O\cdots OH\end{array}\right.\end{array}$$

The reaction, of which this body is the result, is represented by the following equation † :—

$$C^7H^6O^6 + PCl^5 - 2HCl = C^7H^4Cl^3PO^6.$$

This is the same body which, unpurified, Gerhardt calls the chloride of salicyl,‡ and Chiozza the chloride of chlorobenzoïl,§ or the hydrochlorate of monochlorobenzoic acid. In order to determine rigorously whether the body produced by Chiozza from salicylic acid was really the same as that which Gerhardt and I have obtained from the oil of gaultheria, I investigated the action of the perchloride of phosphorus upon the pure acid. The reaction which takes place between the two solid bodies is less violent than when the oil was employed. Nevertheless, in this instance also the action is prompt. After the vapour of hydrochloric acid has passed off, the residue in the flask is identical with that which remains when the oil of gaultheria is employed. These two products distil in identically the same manner, with the same physical appearances, while the products of distillation produce exactly the same results upon analysis.

These products display also entirely the same results in all their reactions.

The terchlorophosphate of salicyl obtained by either process is very soon decomposed by water in the cold, and immediately, upon the application of heat, the products being hydrochloric, phosphoric, and salicylic acids.

Chiozza's monochlorobenzoic acid, which he believes to be produced along with hydrochloric acid in the decomposition of this body, is only salicylic acid || rendered impure by hydrochloric and phosphoric acids.

Chiozza did not succeed in producing the reaction for salicylic acid by the perchloride of iron. Nor is it to be observed till the liquid containing the phos-

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* *Phil. Mag.*, August 1858.

† Couper gives here the equation representing the action of PCl_5 on salicylic acid (of which he speaks a few lines further on) instead of that for the action on gaultheria oil.

‡ *Comptes rendus*, xxxviii. 34.

§ *Annales de chim. et de phys.* [3], xxxvi. 102.

|| Couper is mistaken in this. Chiozza certainly had in his hands chlorobenzoyl chloride and chlorobenzoic acid.

Je me suis assuré, par l'analyse, qu'il se forme véritablement dans cette réaction, de l'acide salicylique et pas de l'acide monochlorobenzoïque. Lorsque le trichlorophosphate de salicyle est rapidement distillé, il se décompose en partie en émettant d'abondantes vapeurs d'acide chlorhydrique. Au-dessus de 300 degrés il passe un corps liquide, qui, lorsqu'on le conserve pendant quelques jours dans un tube fermé, dépose de volumineux cristaux qui renferment :

			Théorie.
Carbone	40,2	39,16	38,44
Hydrogène . . .	2,3	1,96	1,83
Chlore	17,07	...	16,25

Cette analyse, le mode de formation de ces cristaux et surtout leur dédoublement par l'eau que je vais indiquer plus loin me portent à leur attribuer la composition répresentée par la formule suivante :

$$C^{14}H^{4}O^{8}ClPh.$$

Comme cette substance, que je nomme monochlorophosphate de salicyle, se décompose à l'air dont il attire l'humidité et qu'elle est formée d'ailleurs par un liquide bouillant à une température très-élevée, je ne me suis pas arrêté à la pensée de l'obtenir sous une forme plus pure, et j'ai dû me contenter de l'analyse précédente.

phoric acid is separated from the crystals of salicylic acid, but as soon as this is done, the application of the test gives the intense and characteristic colour produced by the acid in question. An analysis which I have made confirms this result.

0·301 grms. of these crystals, expressed between folds of bibulous paper, re-crystallised from water, and dried, upon combustion, gave 0·668 grms. of carbonic acid, and 0·116 grms. of water.

	Found.	Calculated.
Carbon	60·52	60·86
Hydrogen	4·27	4·34

In another analysis 0·2205 grms. of substance gave 0·4885 grms. of carbonic acid, and 0·0875 grms. of water, which, calculated, gives—

60·42 % for carbon, and 4·4 % for hydrogen.

This acid agrees also in all its physical aspects with the salicylic acid.

It is evident, then, that those three bodies,—namely, the chloride of salicyl of Gerhardt, the chloride of chlorobenzoil, and the chlorobenzoilic acid of Chiozza, are not yet known.

When the terchlorophosphate of salicyl is quickly distilled, hydrochloric acid is given off in considerable quantity, while the body, at the same time, acquires a dark colour. The last portion of the product of this distillation, which passes at a temperature above 300° Cent., being allowed to stand for a day or two in a closed tube, deposits large crystals, which, having been pressed between folds of bibulous paper, and submitted to analysis, gave the following results :—

1°. 0·3565 grms. of substance gave 0·5255 carbonic acid, and 0·074 grms. water.

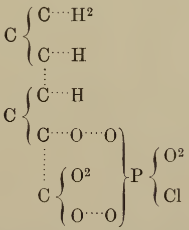
2°. 0·57 grms. of substance gave 0·826 grms. carbonic acid, and 0·101 grms. of water.

1°. 0·255 grms. of substance gave 0·176 grms. of chloride of silver.

Compared with the crude formula $C^7H^4O^8ClP$, these results will be :—

	Found.		Calculated.
	I.	II.	
Carbon	40·2	39·16	38·44
Hydrogen . . .	2·3	1·96	1·83
Chlorine . . .	17·07	...	16·25

The rational formula is—



$$\begin{array}{l} C\left\{\begin{array}{l}C\cdots H^2\\ C\cdots H\end{array}\right.\\ \vdots\\ C\left\{\begin{array}{l}C\cdots H\\ C\cdots O\cdots O\end{array}\right.\\ \vdots\\ C\left\{\begin{array}{l}O^2\\ O\cdots O\end{array}\right. \end{array}\left.\vphantom{\begin{array}{l}a\\a\\a\end{array}}\right\}P\left\{\begin{array}{l}O^2\\ Cl\end{array}\right.$$

The monochlorophosphate of salicyl being a body which is quickly decomposed by exposure to the air, and only to be obtained from a liquid passing at an exceedingly high temperature, I did not think it easily possible to obtain a purer body, and have contented myself with the above analysis. Although these analyses might in themselves leave some doubt as to the composition of the body, still, when taken in

L'action lente que l'humidité exerce sur les produits à la fois chlorés et phosphorés que je viens de décrire confirme la composition que je leur attribue. Lorsqu'on les expose à l'air, ils en attirent peu à peu la vapeur d'eau ; le chlore qu'ils renferment se combine à l'hydrogène, et est remplacé par de l'oxygène. Il se forme ainsi un acide nouveau, que je nomme *acide phosphosalicylique*, et dont la composition est exprimée par la formule

$$C^{14}H^{7}PhO^{12}.$$

Ce produit, qui est solide, a donné à l'analyse les résultats suivants :

	Expériences.	Théorie.
Carbone	38,05	38,53
Hydrogène	3,39	3,21
Phosphore	14,48	14,22

Il prend naissance en vertu des réactions suivantes :

$$\underbrace{C^{14}H^{4}Cl^{3}PhO^{6}}_{\text{Trichlorophosphate de salicyle.}} + 6HO = 3HCl + \underbrace{C^{14}H^{7}PHO^{12}}_{\text{Ac. phosphosalicylic.}}$$

$$\underbrace{C^{14}H^{4}ClPhO^{8}}_{\text{Monochlorophosphate de salicyle.}} + 4HO = ClH + C^{14}H^{7}PhO^{12}.$$

L'acide phosphosalicylique est un acide tribasique. On peut l'envisager comme une combinaison conjugée d'acide phosphorique et d'acide salicylique

$$PhH^{3}O^{8} + C^{14}H^{6}O^{6} = C^{14}H^{7}PhO^{12} + 2HO.$$

Les expériences que je viens de décrire sommairement ne s'accordent pas en tous points avec les observations qui ont été publiées sur le même sujet par MM. Gerhardt,* Chiozza,† et Drion.‡ Elles semblent en particulier jeter quelques doutes sur l'existence du chlorure de salicyle de M. Gerhardt, produit qui n'a jamais été analysé. Nous ferons remarquer d'ailleurs que la formation de ce produit par l'action du perchlorure de phosphore sur l'acide salicylique ou sur l'huile de gaulthéria devrait être accompagnée de celle du chloroxyde de phosphore. Or, dans les réactions dont il s'agit il ne se forme que des traces de cette substance, comme l'indiquent d'ailleurs les auteurs que nous venons de citer. Les divergences que nous signalons tiennent-elles à quelque circonstance fortuite ou à des conditions particulières dans lesquelles se sont placés les observateurs, c'est ce que de nouvelles expériences devront décider.

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* *Comptes rendus*, t. xxxviii. p. 34.

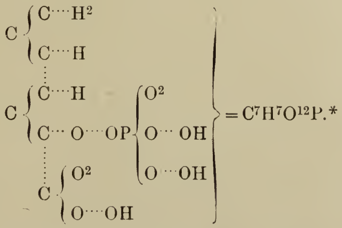
† *Annales de Chimie et de Physique* (3e série), t. xxxvi. p. 102.

‡ *Comptes rendus*, t. xxxix

connection with a combinate which I am about to describe, and which is produced from the monochlorophosphate of salicyl, as well as from the terchlorophosphate, I think I may be warranted in ascribing definitely to it the above formula.

This compound is produced by the exposure to the atmosphere of the bodies just mentioned. The chlorine contained in them decomposes the water of the atmosphere combining with an equivalent of hydrogen, while the oxygen is taken up by the bodies in question in replacement of the chlorine. This new oxygen, however, enters into the state in which it is found in acids, and has a great affinity for the oxygen of water and bases. It therefore attracts the water of the atmosphere, and the combinate becomes an hydrated acid.

This body being submitted to analysis, gave results according with the rational formula—



$$\left.\begin{array}{l} C\begin{cases} C\cdots H^2 \\ C\cdots H \end{cases} \\ \quad\vdots \\ C\begin{cases} C\cdots H \\ C\cdots O\cdots OP\begin{cases} O^2 \\ O\cdots OH \\ O\cdots OH \end{cases} \end{cases} \\ \quad\vdots \\ C\begin{cases} O^2 \\ O\cdots OH \end{cases} \end{array}\right\} = C^7H^7O^{12}P.^*$$

1°. 0·2845 grms. of substance gave 0·397 grms. of carbonic acid, and 0·086 grms. of water.

0·1785 grms. of substance gave 0·103 grms. of the pyrophosphate of magnesia.

	Found.	Calculated.
Carbon	38·05	38·53
Hydrogen	3·39	3·21
Phosphorus	14·48	14·22

This phosphosalicyclic acid is a tribasic acid, and forms insoluble salts with baryta, lead, and silver, containing three equivalents of these metals.

I propose taking into consideration more fully the constitution of salicylic acid in a subsequent communication. The formula here given of that body may be in the meanwhile suggestive.

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* Couper has here for phosphorus the symbol "Ph" as throughout the French paper. Elsewhere in English he uses "P".

(*Issued separately April* 30, 1909.)

$\overset{+}{Na}\ \overset{-}{Cl}$ [illegible] $C_2H_4O_2$

$+$ $+$

$\overset{+}{Na}$ $+$ $H\ Cl$

$Na\ H$

[illegible] $Au\ Cl_3$

[illegible]

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